ISOTOPES AND RADIATION TECHNOLOGY

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Radioisotopes: 1980

By A. F. Rupp

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Isotopes and Radiation Technology
P. S. Baker, A. F. Rupp, and Associates
Isotopes Information Center, Oak Ridge National Laboratory

Nuclear Safety
Wm. B. Cottrell, W. H. Jordan, J. P. Blakely, and Associates
Nuclear Safety Information Center, Oak Ridge National Laboratory

Reactor and Fuel-Processing Technology
Argonne National Laboratory

Reactor Materials
E. M. Simons and Associates
Battelle Memorial Institute

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Isotopes and Radiation Technology

is a Technical Progress Review prepared by the Isotopes Information Center, Oak Ridge National Laboratory, at the request of the Divisions of Technical Information and Isotopes Development, U. S. Atomic Energy Commission. This Review is intended to assist those interested in keeping abreast of significant developments in the fields of isotopes and radiation technology. It is not a comprehensive review of all literature published in this field during a given quarter; rather, it is a mechanism for presenting concise, selected reviews of information on subjects of prevailing Commission interest as it becomes available.

This Review attempts to relate the published results of research and development sponsored by the Division of Isotopes Development to significant developments in radioisotopes and radiation technology, as reported in the world literature. Coverage includes isotope production and development, isotope technology development, isotope applications technology, process radiation development, and radiation processing of food and medical supplies.

In addition to reviews of current literature and special review articles dealing with specific isotopes, facilities, and applications, this publication occasionally contains feature articles prepared by recognized experts on specific topics of current interest. Critical evaluations and interpretations presented are those of the editors and invited reviewers; therefore readers are encouraged to consult the original references in order to obtain all the background of the work reported and the interpretation of the results given by the original authors.

The subject headings listed below have been adopted to help maintain continuity and order, from one issue to the next, in the material reviewed. All reviews, except Feature Articles, will be arranged under these headings; but any one issue will not necessarily contain all the headings.

Isotope Production and Development
Isotope Technology Development
Food Irradiation
Process Radiation Development
Source Development
Isotopic Power Development
Applications in Life Sciences
Safety
Isotopes Around the World
Miscellaneous

P. S. Baker, Robert H. Lafferty, Jr., Martha Gerrard, R. E. Greene, F. E. McKinney, Joan E. Carden, and F. J. Miller, *Editors*
A. F. Rupp, *Adviser*

Oak Ridge National Laboratory

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FEATURE ARTICLE

Radioisotopes: 1980*

By A. F. Rupp†

Abstract: We may expect a slow, steady growth in the use of radioisotopes for medicine, industry, and research, but with no spectacular jump in rate during the next decade. The use of large amounts of radioisotopes for radiation processing and isotopic power will become increasingly price dependent, growth curves being modified by competitive devices, processing economics, and actions taken by the safety regulatory bodies. In short, production and utilization of radioisotopes are now a small but mature business, responding to the usual economic forces of supply and demand.

In taking a look forward in the radioisotopes business toward 1980, it would be well also to look backward a period of years to note the amount and kind of progress made since about the time of the First Geneva Conference in 1955. The number of radioisotope-production sites throughout the world has increased markedly since that conference. Commercial radioisotope production in the United States has increased to the point where most of the commonly used isotopes, such as ^{131}I, are produced in privately owned reactors and processing facilities.[1] The neutron fluxes available for radioisotope production have increased steadily from 10^{11} to $\sim 10^{15}$ n/(cm^2)(sec). Cobalt-60 for use in irradiators has gone from the kilocurie level to the megacurie level, with the specific activity increased[2] from 5 to 10 curies/g to as high as 700 curies/g (Ref. 3). Fission-product ^{137}Cs, ^{90}Sr, and ^{147}Pm, which were just starting to be separated at the ORNL Fission Products Plant in 1955, are now separated and packaged in megacurie quantities per year.[4]

Nuclear medicine, industrial applications, instrumentation, and irradiation techniques have all developed during the past decade at a pace greater than would be expected in a new technology that is fairly difficult to relate to everyday life. Looking back, it seems that progress in radioisotopes work has been good, especially when one considers the relative amounts of time, attention, and money given to the two related fields—nuclear power and radioisotope technology.

Radioisotope Production

Turning now to the decade ahead, let us consider first the availability of raw materials—i.e., radioisotope production. Two kinds of radioisotope production are readily apparent: (1) relatively small quantities, highly purified, of almost every known radioisotope for nuclear medicine and research and (2) megacurie quantities of certain radioisotopes—^{60}Co, ^{137}Cs, and ^{90}Sr—for radiation processing and isotopic power.

Nearly two hundred radioisotope preparations are offered by ORNL and other production centers around the world. While research and development continue to make available newer species (e.g., ^{123}I and ^{125}I, supplementing the older ^{131}I), it is probable that relatively few new radioisotopes will be forthcoming in the next decade for the simple reason that the territory has been pretty well explored, particularly for neutron-excess nuclides. It is to be expected that the newer radioisotopes in the future will come from the lists of neutron-deficient or transplutonium nuclides.

In nuclear medicine, general scientific research, and industrial applications, the demand for radioisotopes has been markedly affected by two outside influences: (1) the ever-increasing pressure from safety people to reduce the amounts of radioactive materials used and (2) the ever-increasing sensitivity and precision of detection instruments, which allow smaller amounts of radioisotopes to be used. In medical diagnosis the desired allowable radiation dose is as near zero as possible. This attitude has resulted in interest in nuclides, such as ^{123}I, which emit no beta radiation to injure surrounding tissues when deposited in the body.[5,6] Shorter and shorter half-life nuclides are being employed; this local production of radioisotopes is needed at clinics, using reactors, radioisotope generators (short-lived daughters from long-lived parent radioisotopes), and especially cyclotrons, which have a wide range of radioisotope-production potential. In nuclear medicine

*Updated version of ORNL-P-2847, which was translated into German for publication in *Atomwirtschaft*, 12(6): 301-303 (1967).

†Director of the Isotopes Development Center, Oak Ridge National Laboratory, Oak Ridge, Tenn.

and in industrial control, I would expect the use of generators and cyclotrons to increase markedly in the next decade.

Extending the concept of "using radioisotopes without radiation," the spiking of systems for diagnostic procedures or industrial control with certain stable nuclides, followed by activation of samples removed from the system, will increase because of the aforementioned safety considerations. Devices such as americium–curium–beryllium neutron sources, spontaneous fission sources such as berkelium, or compact, high-reliability electric neutron generators should grow in demand.

Production in Reactors

Reactor neutron fluxes used at large-scale radioisotope-production sites will probably not grow much beyond the maximum 5×10^{15} n/(cm^2)(sec) now available. Reactors become prohibitively expensive to build and operate as one approaches the 10^{16} n/(cm^2)(sec) level, and one can hardly justify, on a purely economic basis, the operation of more than one or two reactors in the world even at the 10^{14} to 10^{15} n/(cm^2)(sec) level for radioisotope production alone. It is probable that radioisotope production will always be carried on as an adjunct to the operation of reactors for other purposes, such as nuclear research and development or power production. Power reactors, which have neutron fluxes of about 10^{13} n/(cm^2)(sec) and in which there is limited access to irradiation spaces, are not particularly well suited for making small quantities of many different kinds of high-specific-activity radioisotopes. However, it is quite probable that much of the large-scale radioisotope production for ^{60}Co, fission products, and transuranium elements will be done in power reactors specially designed or adapted for irradiation of radioisotope target materials.

Production in Accelerators or by Nuclear Explosions

It is probable that extraordinary fluxes will be available from new types of accelerators now being studied or from controlled nuclear explosions, which may be used for radioisotope production. Machines such as the suggested[7] ORNL Separated Orbit Cyclotron will accelerate heavy currents of protons to 800 Mev. The beam can be extracted efficiently at intermediate energy levels for production of neutron-deficient isotopes, or the main beam can interact with an appropriate target and neutron moderators to give a reasonable volume with thermal-neutron flux in excess of 10^{15} n/(cm^2)(sec). Some experiments have also been done on utilizing the highly concentrated pulses of neutrons developed by underground nuclear explosions. Although the neutron pulses have a duration of only a few microseconds, multiple neutron-capture reactions occur that cannot otherwise be achieved. Of course, the use of neither multimillion dollar cyclotrons nor nuclear explosions could be economically justified solely for radioisotope production. However, radioisotope targets will no doubt be irradiated in intense nuclear beams from sources of this kind to produce unusual radioisotopes for research.

Radioisotope Markets

The markets for ordinary radioisotope preparations (other than for research, or made in on-site devices, or for large-scale irradiators and power devices) should not be expected to grow in the next decade at the rate experienced since 1946. New industrial uses are developing slowly because of management's lingering fears of radioactivity, a general scarcity of aggressive inventors in the field, and competition from a multitude of electronic devices utilizing microwaves, sonic effects, etc. The small increase in use for medical diagnosis and industrial devices has not produced a significant rise in quantity demand for radioisotopes because newer detection and measuring instruments often decrease the amount of radioactivity required by factors of 100 to 1000.

The only prospects for large-scale use of radioisotopes are for irradiation (primarily gamma radiation) and isotopic power (primarily alpha and beta radiation). In this case, millions of curies will be required, but the markets are extremely price-sensitive; radiation processes are subject to heavy competition from electrical machines; and isotopic fuels can compete against other fuels only for very unusual applications, such as in deep space and underseas.

The radioisotopes to be used on a large scale have now been pretty clearly identified. Cobalt-60 and ^{137}Cs are the only ones being considered for the big gamma irradiators; ^{238}Pu, ^{90}Sr, and ^{147}Pm are the primary contenders for isotopic power. However, chiefly because of the limited supply of ^{147}Pm and ^{238}Pu, a number of other radioisotopes are being considered for isotopic power or to meet a particular specification: ^{244}Cm, ^{170}Tm, ^{171}Tm, ^{144}Ce, ^{60}Co, ^{204}Tl, and ^{210}Po.

While the bulk of the ^{60}Co production in the United States and Canada at present is in production or research reactors, some cobalt is being introduced into power reactors,[8] and one would presume that this may be the primary ^{60}Co supply source by 1980. Cesium-137 and ^{60}Co are quite competitive with each other. Being a true by-product, ^{137}Cs will be built up in great quantities from power-reactor fuel processing, whether we want it or not. Probably ^{137}Cs will eventually be the primary source of gamma radiation in cases where the intensity and hardness (0.66 Mev) of the gamma-radiation field are adequate. There is some fear that the long fuel cycles of power reactors will produce low-quality ^{137}Cs (low specific

activity, high ^{134}Cs content); this will no doubt be a problem for designers of irradiators. It may be possible to use 65-day $^{95}Zr-^{95}Nb$ (its 0.6-Mev radiation matches that of ^{137}Cs), a fission product available in enormous quantities from processing of short-cooled fuel to augment ^{137}Cs irradiators during high-demand periods. Cesium-137 and other fission products of high quality could be produced from continuous-processing reactors, such as ORNL's proposed molten salt breeder reactor (MSBR). The demand for certain fission products may eventually exert some influence on the choice of power-reactor type toward the MSBR type because of the increased value of high-quality fission products. The proposed circulating-fuel breeder reactor, in my view, is a specialized sort of dual-purpose power and radioisotope-production reactor.

In addition to producing ^{60}Co and fission products, power reactors will become the primary source of target material for ^{238}Pu and ^{244}Cm production—i.e., ^{237}Np and ^{243}Am. It is not yet clear whether the ^{237}Np and ^{243}Am will be further irradiated in power reactors after isolation, since the neutron flux is too low for good economy. Neptunium-237, for example, can be converted most efficiently to ^{238}Pu by close coupling between irradiation and chemical processing, or by continuous irradiation and processing. Such systems may be adapted to existing reactors, but it is probable that the specially designed, high-flux reactors will be used eventually for this purpose.

While looking into the future of isotopes, I should also call attention to the radioactive gas ^{85}Kr and to the large quantity of stable xenon and other potentially valuable stable fission-product elements that will be produced in the large nuclear power industry in the future. For example, it is estimated that 10^6 Mw-years of energy production would produce 9 million liters of stable xenon, 20 thousand lb of mildly radioactive technetium, and 6 thousand lb of virtually nonradioactive palladium—all potentially valuable elements in tomorrow's world of scarce raw materials.

Projections for pricing radioisotopes that one sees for the future show a steady decline, but there will be a leveling off as the cost of packaging, handling, and shipping radioisotopes becomes the controlling factor. Reductions in the cost of ^{238}Pu and ^{244}Cm may be expected as target materials become available as by-products from power reactors. However, fission products and ^{60}Co, now priced quite low in large quantities, will probably not decrease a great deal in price over the years. (MG and PSB)

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Section I

Isotopes and Radiation Technology

Isotope Production and Development

Solvent Extraction of Fission Products, II. Cesium*

By F. J. Miller

Abstract: The liquid–liquid solvent extraction of fission-product cesium is discussed here, chiefly from the standpoint of recovery of a potentially valuable radioisotope from nuclear energy fuel-reprocessing waste solutions. The basic principles covering the majority of extraction schemes are presented in detail. Specific extraction schemes—the dipicrylamine, tetraphenylboride, polyhalide, and substituted phenol, synergistic extraction, and chelation with subsequent extraction—are given with specific references. Some consideration is given to the safety of the solvents used. An attempt is made to correlate the extraction schemes with theory and to indicate a possible future line of work.

Cesium radioisotopes as potentially valuable, reclaimable fission products have attracted the attention of nuclear energy process chemists[2,3] since 1955. Only recently Cochran and Cunningham[4] discussed some of the economic aspects of cesium mixtures for large radiation sources. In connection with reducing capital requirements and operating cost for large irradiation plants, fission-product cesium offers certain advantages—abundant supply, potentially low cost, and flat depth-dose distribution. Disadvantages are the limited specific activity resulting from the presence of nonradioactive cesium fission-product isotopes in the final mixture and the lower effective gamma energy per curie of ^{137}Cs as compared with ^{60}Co.

If the fuel from a pressurized-water power reactor is processed within a year after discharge, the cesium composition, assuming an irradiation of 2.5×10^4 Mwd/metric ton, would be

Stable	^{133}Cs	852 g/metric ton
2.07 years	^{134}Cs	101 g/metric ton
2.0×10^6 years	^{135}Cs	406 g/metric ton
30 years	^{137}Cs	950 g/metric ton

If the entire cesium fraction is separated and converted to CsCl 1 year after discharge, the chloride would contain 29.3 curies of ^{137}Cs and 31.3 curies of ^{134}Cs per gram. The average gamma energy per disintegration of ^{137}Cs is 0.562 Mev resulting in a gamma flux of 2.157×10^{10} Mev per second per curie of ^{137}Cs. The average gamma energy per disintegration of ^{134}Cs is 1.565 Mev for a gamma flux of 5.79×10^{10} Mev per second per curie.

Cochran and Cunningham[4] also presented data to show further savings that would accrue from the early processing of the reactor fuels so that use could be made of ^{134}Cs as well as ^{137}Cs. Cost studies indicate that cesium sources would have a useful life of some 30 years.

The cost of the material depends to a large degree on the economics of separation and purification from accumulated waste materials derived from reprocessing reactor fuels. Solvent extraction has been investigated as a process uniquely adaptable to the conditions of handling highly radioactive material safely and with reasonable cost.

In the present discussion, not only extraction procedures of interest to the nuclear energy industry but also some that are solely of analytical concern are included to show the development in an orderly manner of the solvent extraction of cesium.

Principles

When looking at the literature concerning cesium extraction for the first time, one observes a confusingly large number of extractants and organic solvents in use. The development of these appears to be based on no rationale other than the empirical development from classical gravimetric procedures with organic solvents commonly found in an analytical laboratory. Possibly in the early stages of search

*This is the second in a series of articles devoted to the liquid–liquid extraction of potentially valuable radioisotope fission products from solutions generated in the processing of spent nuclear fuels to recover uranium and plutonium values. The previous article[1] pointed out the accumulated large amounts of cesium in stored Hanford fission-product wastes and the increase anticipated from new power-installation facilities.

many procedures were developed in just such a manner. But there are basic principles that govern the extraction of such ions as Cs^+, and these principles may be used not only to elucidate procedures developed empirically but also to facilitate and guide a scientific investigation of the problem to a fruitful culmination. Consideration of these guiding principles, as discussed by Slater,[5] is requisite to the understanding of the various extractant schemes in current or contemplated use.

Cesium, typical of the alkali metals (Li, Na, K, Rb, and Cs), shows only a very slight tendency toward the formation of coordination complexes or compounds; the approach generally taken therefore is to form an extractable species of the ion-association type. An ion-association complex is an uncharged compound formed in solution by association of oppositely charged ions in pairs or larger aggregates. The forces holding the combination together are essentially electrostatic in nature, and the usual chemical bonding is not attained; however, the formation and dissociation of the complex follow the law of mass action:

$$X^+ + Y^- \rightleftharpoons (X^+, Y^-)$$

$$K = \frac{[(X^+, Y^-)]}{[X^+][Y^-]}$$

where X^+ and Y^- are oppositely charged ions, and K is the equilibrium constant. The constant K can be calculated, according to Bjerrum,[6] who predicted the existence and behavior of ion-association complexes, from the equation

$$K = \frac{4 \times 10^{-3}\, \pi N e^2}{DkT}\, Q(b)$$

where N = Avogadro's number
e = unit of electron charge
D = dielectric constant
k = Boltzmann constant
T = absolute temperature
$b = e^2/aDkT$

The distance between the centers of charge of the paired ions when in contact is represented by a, and Q is a function of b such that K decreases as a increases.

The constant K should decrease as T increases; however, the product DT decreases because D decreases rapidly with increase in T. If the distance between the ionic radii does not change appreciably with change in solvent, K will vary from solvent to solvent as an inverse function of D.

The solvent extraction of an ion-association complex may be represented by the simplified equilibriums

$$X^+_{(aq)} + Y^-_{(aq)} \rightleftharpoons (X^+, Y^-)_{(aq)} \rightleftharpoons (X^+, Y^-)_{(org)} \rightleftharpoons X^+_{(org)} + Y^-_{(org)}$$

where X^+ represents the univalent metal ion Cs^+, Y^- is any one of a number of singly charged anions, and (aq) and (org) represent the aqueous and organic phases, respectively. Extraction of X^+ can be favored by strengthening the association of X^+ and Y^-. Lowering the dielectric constant of the aqueous phase by increasing its salt concentration or organic solvent solubility is a means to the desired end.

Increasing $[Y^-]$ also favors formation of (X^+, Y^-) because of the mass-action effect. Extraction of X^+ can also be increased by facilitating the dissociation of the ion-association complex in the organic phase; the use of an organic solvent of high dielectric constant is therefore useful. If the extractant is a large organic anion that has some similarities to the organic solvent, the extraction of X^+ will also be enhanced.

The extraction coefficient, representing the ratio of X^+ concentration in the organic phase to that in the aqueous phase, will tend to be larger for very dilute solutions of $X_{(aq)}$ than for more concentrated solutions because the greater loading of the organic phase represses the equilibrium

$$(X^+, Y^-)_{(org)} \rightleftharpoons X^+_{(org)} + Y^-_{(org)}$$

Reversal of this situation may occur at higher concentration because of the formation of aggregates larger than the ion pair:

$$A(X^+, Y^-)_{(org)} \rightarrow (X^+, Y^-)_{A(org)}$$

But since this occurs most readily when one of the ions is small and the dipole moment of the complex is large, it is not likely in the case of cesium extraction.

The statement that the use of an organic solvent of high dielectric constant favors the extraction of an ion-association complex appears to be paradoxical. Water, itself, is a solvent of high dielectric constant, 80.36, as compared with 35.74 for nitrobenzene (Hasted's[32] value for water is 78.5). Slater asks the question, "In view of this, why should extraction from aqueous solution take place at all?" A discussion of this question is outside the scope of the present article, but it has been analyzed by Friedman[7] and further discussed by Goble and Maddock.[8] It may be stated that extraction will take place only if the anion present in the aqueous phase is large. From consideration of the electrostatic contribution alone, the extraction of cesium or any alkali-metal cation from aqueous solution is not favored. But cesium would be less likely to be held back by water dipoles than the other alkali metals because of its larger effective ionic radius and crystal ionic radius. The net effect is that the unit positive charge is diffused over the surface of a larger volume and thus holds less attraction for the water dipole. This result is in sharp contrast with that for the Li^+ ion, which has the same

charge but an effective ionic radius of less than half that of Cs^+. Lithium ion in water is consequently surrounded by a hydration sheath of water molecules.

Organic solvents having a center of charge close to the surface of the part of the molecule that would face the extractable ion would be expected to be good solvents because the effective distance between the charge centers would be less.

The energy necessary to transfer the ion-association complex from the aqueous phase to the organic must, in the last analysis, be derived from the free energy released by the re-creation of the hydrogen-bonded water structure following removal of the extracted complex. The larger the cavity left in the water structure by the removal of the complex, the greater the number of re-formed hydrogen bonds and consequently the more favorable the overall free-energy change for the solvent extraction. Thus the use of as bulky an anion as possible with the relatively large cesium cation is dictated from free-energy considerations.

Siekierski[9] considers the situation as somewhat more complex. There is at present no quantitative theory of the extraction process. It is not possible to predict quantitatively the values of partition coefficients, and even the effect of changing one of the variables influencing extraction is difficult to predict. The lack of a quantitative theory is mainly due to the fact that the overall change in the free energy following an extraction process is the sum of the partial changes corresponding to such processes as dehydration, complex formation, or solvation in the organic phase. Now, the free-energy change for every partial process is greater by one or two orders of magnitude than the free-energy change for the overall process. Thus two ions differing only slightly in their chemical properties can differ greatly with regard to their extractive properties under the same conditions. A difference of 5.5 kcal in the free energy of hydration of two cations is equivalent to a ratio of 10^4 for the partition coefficients, which is, in practice, just the difference between a very well- and a non-extractable species. A difference in hydration energies of the order of several kilocalories might be, in turn, equal to only a few percent of the total hydration energy of the extracted cation. Since exact thermodynamic data are not available, partition coefficients cannot be calculated. Semiquantitative predictions of the effects of changing one of the variables can be made, thus reducing the amount of experimental work necessary.

Despite Siekierski's amplification, Slater's discussion of the underlying theory leads to the conclusions that (1) of all the alkali metals, cesium extraction is most favored; (2) a coordination complex or chelate compound is not to be anticipated, but an ion-association pair may possibly be formed; (3) for the formation of a suitable ion pair, a singly charged inorganic or organic anion of as large an ionic radius as possible is desirable; (4) the organic extractant should be structurally similar to the organic solvent; and (5) for the organic solvent, an organic compound of as high a dielectric constant as possible should be used. It can further be inferred that, since the possible inorganic or organic extractants are classified as weak acids, extraction will take place only at nearly neutral or slightly alkaline *p*H. How well these theoretical conclusions coincide with experiment may be judged from the specific extraction schemes discussed in the following section.

Specific Extraction Schemes

DIPICRYLAMINE AS EXTRACTANT

Bray and Roberts[10] at Hanford Laboratories have reported on the dipicrylamine extraction into nitrobenzene of cesium from Purex[1] wastes. Dipicrylamine (2,2′,4,4′,6,6′-hexanitrodiphenylamine), commonly referred to as DPA, was found to be a very effective and highly selective extractant for cesium. Bray and Roberts assume that the extractability of Cs–DPA is the result of ion-pair association, forming an extractable complex. The ionization of dipicrylamine by loss of the amine hydrogen results in the formation of a large negative ion, which can form an ion pair with the large (effective ionic radius 2.54 A), poorly hydrated Cs^+ ion.

A comparison of the radii of the alkali metals (Table 1) shows the variation among them. The value

Table 1 IONIC RADII FOR THE ALKALI METALS AND EQUILIBRIUM CONSTANTS FOR THE Cs–DPA REACTION*

Y	Ionic radii, A		Equilibrium constant, K_Y
	Crystal	Aqueous	
Cs^+	1.69	2.54	2×10^6
Rb^+	1.48	2.33	4.3×10^5
K^+	1.33	2.18	8.5×10^4
NH_4^+	1.43		2.4×10^4
Na^+	0.95	1.80	1100
Li^+	0.60	1.45	150

*Taken from Ref. 10.

of the equilibrium constant, K_Y, for the Cs–DPA reaction in nitrobenzene was obtained through a series of tracer experiments with ^{137}Cs and ^{22}Na. If the logarithms of the equilibrium constants are plotted against the crystal ionic radii or the effective ionic radii in aqueous solution, a linear correlation is obtained with only the ammonium ion deviating. Since the ammonium ion is only a pseudo alkali metal, the deviation is not surprising. The correlation helps confirm the simple ion-pair mechanism concept. It is thought that, when ionization of the hydrogen ion from the amine nitrogen has taken place, as would happen in a solution of high *p*H, all three nitro groups (NO_2^-) of one ring are now equivalent and the single charge is dispersed or "smeared out" over the entire ring. Such a large, dispersed charge is energetically suitable

for ion-pair formation with the Cs^+ ion, which has a positive charge also dispersed over a large volume. The efficiency of alkali-metal extraction with DPA is a direct function of the radii of the alkali metals.

The compound DPA can be regarded as similar to the aromatic NO_2^- compounds that possess ionizable hydrogen ions and have an acid strength greater than that of water. These pseudo acids have the capacity to form salts with strong bases in aqueous solutions. When treated with aqueous alkali, the yellow baso-form of DPA is converted to a red anion, which forms an organic-soluble species with cesium. The addition of dilute acid to the organic phase regenerates the baso-form of DPA and releases the Cs^+ ion to the aqueous phase.

Diluent for the Organic Phase. The choice of an organic solvent for a process involving the large-scale extraction of highly radioactive materials is much more restrictive than that offered to an analytical procedure or an academic study. The factors of chemical and radiation stability, cost, availability in quantity, insolubility in the aqueous system, and the necessity for a high dielectric constant must be taken into account. Nitrobenzene was originally suggested by Moore.[11] Slater pointed out that a high-dielectric-constant solvent should promote extraction of ion-pair complexes by favoring ionization in the organic phase. The fact that DPA is a large organic anion similar to the organic solvent should enhance the extraction of the cation. Studies of the DPA–nitrobenzene system by Kyrs et al.[12a,b,c] and by Smit[13] have also confirmed the aptness of the choice of nitrobenzene as a solvent for dipicrylamine.

The extraction mechanism for Cs–DPA into nitrobenzene is predicated on the ionization of DPA at high *p*H. The effect of *p*H on the transfer from the aqueous system was tested by measurement of distribution ratios at *p*H's ranging from 1 to 12. The organic phase was 0.01*M* DPA in nitrobenzene; the aqueous system was either 1*M* NaCl plus 0.001*M* CsCl in HNO_3 with *p*H gradually raised by addition of NaOH, or a synthetic waste solution that also contained formaldehyde. Above *p*H 5, distribution ratios favor cesium extraction. Equally important as extraction, stripping of the cesium from the organic phase may be accomplished by equilibration with a dilute aqueous HNO_3 solution up to 1*M*; beyond this a reversal takes place. The reversal at high acid is due to cesium extraction with nitrobenzene rather than DPA. Separation factors from the other alkali metals — rubidium, potassium, and sodium — are 6, 28, and 2500, respectively, over a wide range of sodium concentrations. The cesium distribution ratio has an inverse dependence on Na^+ concentration with a slope of −1 over a wide range. A solvent-loading study with DPA showed that saturation was reached with a DPA-to-cesium ratio of 1:1.

An especially interesting finding reported by Bray and Roberts[10] is that DPA is destroyed by a radiation dose of 2×10^8 r. The radiation stability would thus be sufficient for the purpose intended, and the gradual destruction of the DPA would ensure that no dangerous buildup of organic would occur in the storage tanks.

For an economically feasible process, the conservation of both diluent and extractant is important. Studies showed that the solubility of nitrobenzene in water was 1.9 g/liter and from 2 g/liter in 0.5*M* HNO_3 to 18.5 g/liter in 10*M* HNO_3. In alkaline solutions the solubility of nitrobenzene decreases sharply with increasing cation concentration and reaches a value of 0.15 g/liter in 9*M* NaOH.

Bray and Roberts conclude that the extraction of cesium with DPA in nitrobenzene is not only feasible for reclaiming cesium from reactor fuel-reprocessing waste solutions but should also be of value in recovery of cesium from ores and brines.

TETRAPHENYLBORIDE AS EXTRACTANT

In one of the earliest extraction schemes, McKenzie and Schulz[14] suggested the use of sodium tetraphenylboride $NaB(C_6H_5)_4$ (abbreviated as NaTϕB) to extract cesium from a 2.5*M* $NaNO_3$ solution at *p*H of 2.5. Irvine and Fix[2] reported the extraction of cesium and rubidium into nitrobenzene with NaTϕB. Finston[15] described an analytical procedure for cesium in which a buffered fission-product solution was extracted with a 0.05*M* NaTϕB–amyl acetate solution. Wischow et al.[16] reported additional findings in cesium extraction from Purex-type waste solutions with NaTϕB in hexone.

Finston's procedure is a simple extraction useful for analytical purposes. The test solution is buffered to *p*H 6, extracted with 0.05*M* NaTϕB in amyl acetate and stripped with 3*M* HCl. Davies and Diggle[17] also described an analytical extraction procedure based on earlier work of Leaf.[18] In the work of Davies and Diggle, cesium was extracted from HNO_3, HCl, or H_2SO_4 solutions of irradiated plutonium or uranium. The cesium was extracted with NaTϕB in amyl acetate from a test solution, buffered to an alkaline *p*H, that contained also sodium ethylenediamine tetraacetate. Interference from radioruthenium was avoided by warming and cooling the solution prior to extraction so as to convert the ruthenium to an unextractable form.

Jenkins and Perkins,[19] at the station in Woolwich, England, also described a similar analytical extraction of cesium; however, they developed their procedure from work described by Handley and Burros,[20] which is a gravimetric method using NaTϕB as a precipitating agent.

The study of Wischow et al.[16] disclosed a useful extraction of cesium with NaTϕB in hexone (methyl isobutyl ketone) from solution over the *p*H range from 3 to 12 with a $NaNO_3$ concentration up to 3*M*. Increasing the NaTϕB concentration in the hexone phase from 0.1 to 0.5*M* increased the extraction

coefficient according to the approximate relation $E = [NaT\phi B]^{2.9-3.5}$. Cesium was extracted as effectively from Purex solution adjusted to 1*M* in tartaric acid at *p*H 6 as from $NaNO_3$ solution. One disadvantage of the NaTϕB extraction was the reported decomposition of aqueous NaTϕB solutions, but stored solutions of NaTϕB showed no decomposition over a 2-week period.

Cesium could not be stripped from NaTϕB–hexone solutions by replacement of the Cs^+ with Na^+, Li^+, NH_4^+, or Al^{3+}, but effective stripping was obtained with dilute solutions of mineral acids. Unfortunately the NaTϕB was converted by acids to a form that on recycle was an ineffective cesium extractant. Treating with caustic did not regenerate the NaTϕB. Obviously the initial cost of NaTϕB ($50 to $180/lb) and its once-through use eliminated NaTϕB extraction as a large-scale process. It remains a useful analytical procedure because here the quantity of NaTϕB used is small.

POLYHALIDES AS EXTRACTANTS

Cesium extraction with polyhalide ions into an organic phase has been successfully demonstrated by Slater[21] at Brookhaven and by Pummery and Moss[22a,b] at Harwell, England. Despite the successful demonstration, the polyhalide extraction has not been considered as a process in the United States because of the anticipated problem of corrosion of the customary stainless-steel equipment by the acidic halide solutions. Nonetheless, halide extraction is important as an almost classic example of ion-pair formation of the extractable species with an inorganic anion.

Polyiodides. Prior to Slater's work, Bock and Hoppe[23] had shown that all the halides of the alkali metals except LiF and LiCl could be extracted in varying degrees into iodine solutions in nitromethane. The use of alkali metals and halogens of higher atomic numbers increased the extraction efficiency. Slater pursued the work further by testing the extraction of tracer ^{137}Cs into a series of organic solvents of relatively high dielectric constant. Such solvents usually showed a better extraction, but the basicity of the solvent also had to be taken into account. Furfural, which has a dielectric constant of 41.9, higher by 7 units than that of nitrobenzene (34.9), showed an extraction coefficient smaller by a factor of 146. The unexpected anomaly was explained by the greater basicity of furfural. Since a basic solvent favors the formation of coordinate bonds, the extraction of ion pairs would not be effective. Slater's work showed that cesium could be extracted from $NaClO_4$, $NaNO_3$, and Na_2SO_4 solutions, all 0.2*M* in NaI, into solutions of 0.2*M* I_2 in nitrobenzene. Cesium extraction coefficients were much greater than those for sodium, and both decreased with increasing salt concentrations. Extraction of cesium from a solution of fixed cesium concentration was a maximum at a NaI concentration of $10^{-2}M$ and decreased sharply with further increase in NaI concentration. Extraction was favored by an increased I_2 concentration in the nitrobenzene and by increasing the volume ratio of organic to aqueous. Effectiveness of extraction was inversely dependent on the temperature. The *p*H of aqueous 0.2*M* NaI equilibrated with 0.2*M* I_2 in nitrobenzene is 4.5. Decreasing the *p*H to 2 had little effect on cesium extraction, but decrease to 1 lowered the extraction coefficient by one-half, and further decrease dropped the extraction coefficient still more.

Aqueous iodine chemistry is far from simple. Slater's explanations of the reactions involved in ion-pair formation and subsequent extraction are stated, probably wisely, as matters of belief rather than as experimentally verifiable statements. Conjecture that is based on a thorough knowledge of the literature coupled with considerable experimental work is, however, worth consideration. The reactions are given as

$$I_{2(aq)} \rightarrow I_{2(org)}$$

$$I_{2(aq)} + I^-_{(aq)} \rightarrow I^-_{3(aq)}$$

$$2I^-_{3(aq)} \rightarrow I^{2-}_{6(aq)}$$

$$Cs^+_{(aq)} + I^-_{3(aq)} \rightarrow (Cs^+, I^-_3)_{(aq)} \rightarrow (Cs^+, I^-_3)_{(org)} \rightarrow Cs^+_{(org)} + I^-_{3(org)}$$

Even more complex polyiodides up to the enneaiodide, I^-_9, are thought to be further involved in the equilibriums. Slater's work demonstrated that polyiodide extraction of cesium from acid-salt solutions and from simulated Purex-waste solution was feasible, and his report gave a reasonable account of the mechanism involved.

Polybromides. Pummery and Moss[22a,b] at Harwell investigated the extraction of cesium with bromides. The results of their macroscale work showed that the distribution coefficient for cesium, D_{Cs}, is inversely proportional to the square root of the aqueous cesium concentration, directly proportional to the aqueous Br_2 concentration, and proportional to the square root of the aqueous bromide-ion concentration

$$\frac{[Cs^+]_{(org)}}{[Cs^+]_{(aq)}} = k \frac{[Br^-]^{1/2}_{(aq)}[Br_2]_{(aq)}}{[Cs^+]^{1/2}_{(aq)}}$$

The ½-power dependence may be explained by dimerization of the Cs^+ in the aqueous phase or by the existence of Cs^+ and Br^- ions in the organic phase. By consideration of the possible equilibriums and the fitting of the experimentally obtained data, Pummery and Moss arrived at the conclusion that cesium and bromine exist as ions in the organic phase and that the bromine species is probably the pentabromide, Br^-_5. A study of the influence of hydrogen-ion concentration on the cesium extraction indicated that in-

creasing amounts of hydrogen ion decrease the cesium extraction; increasing the amounts of ionic salts, e.g., Mg^{2+}, in the aqueous phase decreased the cesium extraction rapidly, but no simple relation between the extraction and salt concentration was found. In summarizing their work, Pummery and Moss state that for the extraction of $CsBr_5$ aqueous solution the partition coefficient, P_{Cs}, may be found from

$$P_{Cs} = \frac{[Cs^+]_{(org)}[Br_5^-]_{(org)}}{[Cs^+]_{(aq)}[Br_5^-]_{(aq)}} \approx 430$$

between the limits

$$10^{-4}M < [Cs^+]_{(aq)} < 10^{-1}M$$

$$10^{-4}M < [Br^-]_{(aq)} < 10^{-1}M$$

$$2 \times 10^{-5}M < [Br_2]_{(org)} < 2 \times 10^{-2}M$$

Hydrogen ion was also found to be extracted into the nitrobenzene in approximate conformity to the expression

$$P_{OH_3Br_5} = \frac{[OH_3^+]_{(org)}[Br_5^-]_{(org)}}{[OH_3^+]_{(aq)}[Br_5^-]_{(aq)}} \approx 1$$

Apparently Pummery and Moss had been stimulated to make the complete study reported in 1962 by the success encountered in cesium extraction from solutions simulating Windscale plant wastes with bromides into nitromethane. For this procedure the extractant was required to function in an aqueous solution 3*M* in HNO_3. The polybromide system was one of very few adequate for this purpose.

OTHER LARGE INORGANIC ANIONS AS EXTRACTANTS

Other investigations[2,3] have been made on the use of a few large inorganic anions such as the hexafluorophosphate ion (PF_6^-), the tetrafluoroborate (BF_4^-) (Ref. 22*a*), and the hexafluoroarsenate (AsF_6^-) (Ref. 22*a*). These efforts are chiefly notable as illustrative examples of ion-pair association complexes with the alkali metals, but because of cost, availability, and precipitate formation, these extractants have never received any great prominence as process extractants.

SUBSTITUTED PHENOLS AS EXTRACTANTS

Horner et al.[24a,b] at ORNL made extensive studies of cesium extraction with substituted phenols. Best results were obtained with *o*-phenylphenol (OPP), 4-chloro-2-phenylphenol (PCOPP), and particularly, 4-*sec*-butyl-2-(α-methylbenzyl)-phenol (BAMBP), and 4-chloro-2-benzylphenol (Santophen-1). According to these authors, alkali-metal extraction may be considered as a cation exchange between an alkali-metal ion, M, and the hydrogen of the phenol, as represented by the general equation

$$aM^+_{(aq)} + bRH_{(org)} \rightleftharpoons [M_aR_bH_{b-a}]_{(org)} + aH^+_{(aq)}$$

where RH is a substituted phenol. One H^+ is released for each Cs^+ extracted, as confirmed by experiments. The stoichiometry as represented by the equation would be expected to be 1 to 1; that is, the coefficients *a* and *b* would be equal to 1. Experiment showed, however, that *b* was ~3 in an extraction of tracer amounts of Cs^+ from an aqueous solution of *p*H 11.7 to 11.8 into diisopropyl benzene.

The phenols are classed as very weak acids so that best extraction is obtained from alkaline aqueous solutions. Conversely, the extracted cesium is easily stripped from the organic phase by very dilute acids. In contact with alkaline (sodium hydroxide) aqueous streams, the phenols are partially converted to sodium phenolates, part of which distributes to the aqueous phase. The loss to the aqueous phase is large for some phenols, e. g., OPP, but very low for others, e. g., BAMBP.

For most phenols, best results were obtained with substituted benzenes, such as diisopropylbenzene, as the diluent. When 4-*sec*-butyl-2-(α-methylbenzyl)-phenol was used, however, cesium extraction coefficients were considerably higher with aliphatic diluents, e.g., kerosene.

Horner et al.[24a] tested the extraction of cesium from simulated and actual waste solutions. Cesium recoveries of 97 to 98% were reported with *o*-phenylphenol, 4-chloro-2-phenylphenol, 4-chloro-2-benzylphenol (Santophen-1), and 4-*sec*-butyl-2-(α-methylbenzyl)-phenol.

Egan, Zingaro, and Benjamin[25] have considered the more basic chemistry of cesium extraction with 4-*sec*-butyl-2-(α-methylbenzyl)-phenol. The useful tools of infrared spectrophotometry, nuclear magnetic resonance, nonaqueous titrimetry, tracer-tracking, and flame spectrophotometry were all used. Accordingly, it can be stated that the first-power *p*H dependence of the cesium extraction shows an extraction reaction involving the exchange of Cs^+ with the H^+ of the phenol. A third-power dependence on reagent concentration was observed, together with a loading ratio of 4 moles of 4-*sec*-butyl-2-(α-methylbenzyl)-phenol per mole of cesium. Before the two observations can be reconciled, the reagent would necessarily have to be polymerized to $\bar{n} = 4/3$, suggesting that multiple equilibriums are operating. From these and other considerations, the following reactions are assumed:

$$2ROH_{(org)} \rightarrow (ROH)_{2(org)}$$

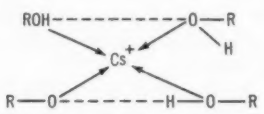
$$Cs^+_{(aq)} + 4ROH_{(org)} + OH^-_{(aq)} \rightarrow CsOR \cdot 3ROH_{(org)} + H_2O$$

$$Cs^+_{(aq)} + 2(ROH)_{2(org)} + OH^-_{(aq)} \rightarrow CsOR \cdot 3ROH_{(aq)} + H_2O$$

An abrupt change in the extraction isotherm at a cesium concentration of 0.25*M* in 1*M* 4-*sec*-butyl-2-(α-methylbenzyl)-benzol and the ease of extraction of all the alkali metals at high aqueous hydroxide-ion concentrations suggest a shift to the equilibrium

$$M^+(H_2O)_{x(aq)} + OH^-_{(aq)} + ROH_{(org)} \rightleftharpoons M^+OR^-(H_2O)_{y(org)} + (x - y + 1)H_2O$$

The proposed basis for the selective extraction of cesium with 4-*sec*-butyl-2-(α-methylbenzyl)-phenol is very much the same as that which Slater suggests for the ion-association extraction of cesium—that is, the small hydration energy that must be overcome, the favorable decrease in free energy resulting from rejection of the large univalent ion by the interrupted aqueous phase, and re-formation of the normal water structure. The extracted species could possibly be only an ion pair, such as cesium phenolate, or a polymer, $Cs^+[RO(ROH)_n]^-$, where n is a small integer. Most investigators rule out the simple ion-pair hypothesis. Another possible structure suggested by the work of Van der Heijde[26] and that of Harlow and Bruss[27] is



which has the Cs^+ ion between pairs of solvating phenols. This structure is in agreement with known data as also discussed by Egan, Zingaro, and Benjamin.[25]

SYNERGISTIC EXTRACTION

The phenol extraction of cesium was studied by Bray[28a,b,c,d] and combined with the use of di-(2-ethylhexyl)-phosphoric acid (HD2EHP) to develop the extraction process known as the CSREX process. Workers at ORNL had reported the extraction of alkali metals with HD2EHP in a preferred order of $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. Bray's contribution was the observation that a mixed extractant of HD2EHP and 4-*sec*-butyl-2-(α-methylbenzyl)-phenol reversed the preference order and made possible cesium extraction at a much lower *p*H than with the use of 4-*sec*-butyl-2-(α-methylbenzyl)-phenol alone. Bray's work further suggests that a phenol-solvated metal salt is formed in the organic phase. His discussion and explanation of the reversibility of the extraction order of the alkali metals is ambiguous; however, he did establish that the species extracted is anhydrous $Cs^+(HD2EHP)(BAMBP)_4$. The alkali metals of smaller ionic radius than rubidium are hydrated and transfer water into the organic phase in inverse ratio to their size.

Rather extensive studies by Keder, Martin, and Bray[29] using titration, freezing-point depression, and infrared measurements do not support the cage structure suggested by Egan, Zingaro, and Benjamin.[25] The structure postulated by the latter would suggest that the phenols are bonded to each other and to the cesium. Keder, Martin, and Bray, in the case of cesium extracted with combined HD2EHP and 4-*sec*-butyl-2-(α-methylbenzyl)-phenol, conclude that the phenols are not bonded to each other and that the phosphate anion is bonded to a phenol rather than directly to the metal ion. The cesium must be bonded directly to the phenol through the phenol oxygen, through the π electrons of the phenol ring or otherwise. The evidence in support of this bonding is lacking, and additional work would be required to establish the structure of the extracted species. Zingaro and Coleman have further considered synergism and the diluent effects in the extraction of cesium by 4-*sec*-butyl-2-(α-methylbenzyl)-phenol.[29a]

Moore, Bray, and Roberts[30] point out the advantage of cesium extraction with 4-*sec*-butyl-2-(α-methylbenzyl)-phenol in the processing of Hanford[1] wastes: the same kerosene-type diluent can be used with 4-*sec*-butyl-2-(α-methylbenzyl)-phenol that is used in the Purex process and in the HD2EHP strontium purification process. The dipicrylamine process previously considered required a high-dielectric-constant solvent such as nitrobenzene, but this is undesirable because of its toxicity and high specific gravity. The CSREX process is also operable at a much lower *p*H than the dipicrylamine extraction. The CSREX process allows extraction of strontium, rare earths, and cesium in a single step in the *p*H range of 3 to 5. The extracted ions can be selectively and individually stripped from the organic phase by varying the *p*H so that separate product streams of strontium, cesium, and rare earths are obtained.

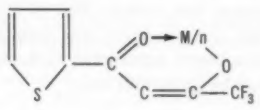
Studies of the CSREX process were discontinued at Hanford owing to severe chemical attack of the phenol (BAMBP) by nitrite ion under relatively high acid conditions used in this process. No attack by nitrite occurs under the alkaline extraction conditions of the ORNL flow sheet.[24a] In a demonstration[24b] of the process with Hanford Purex waste, there was no noticeable degradation of BAMBP in 80 extraction–stripping cycles.

2-THENOYLTRIFLUOROACETONE AS EXTRACTANT

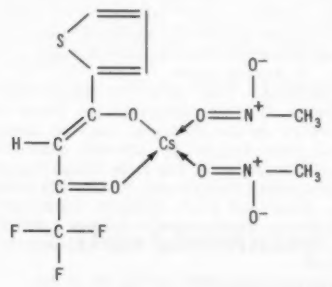
Crowther of South Africa and Moore of ORNL[31] working together at ORNL developed an extraction procedure for cesium that is worthy of comment because of its singular approach. In all previous methods that have been considered, cesium has been extracted as an ion-pair component, essentially a saltlike combination with a weak acid or in the case of BAMBP as a coordination complex. Crowther and Moore propose the extraction of cesium with 2-thenoyltrifluoroacetone (TTA) as a chelate. The idea of forming a chelate

structure with an alkali metal ion is surprising since these ions have almost no propensity for the formation of chelates. The typical chelate compound is formed with multivalent ions, especially those of the transition metals.

TTA reacts with many elements to form un-ionized, organic-soluble chelates of the form



in which M represents a polyvalent metal ion and n the number of available valence bonds. The alkali metals, because of their large size and small charge, form saltlike derivatives of β-diketones that are insoluble in hydrocarbon solvents. These compounds can be solubilized to some extent by the addition of neutral molecules to bring the apparent coordination number up to 4 or 6. A suitable choice of solvent could make possible a liquid–liquid extraction. In the course of the search for a suitable solvent, TTA in hexone was used, and the effect of the addition of even small quantities of Li^+ to the aqueous phase was noted. A dramatic increase in the effectiveness of extraction was observed when the addition of Li^+ to the aqueous phase was combined with use of nitromethane as the organic diluent for the TTA extractant. When equal volumes of 0.5M TTA–nitromethane and an aqueous phase 0.3M in lithium was used, 98% of the cesium was extracted into the organic phase at pH 8.7 in 3 min. The structure of the organic-solvated species in nitromethane, from previous consideration of the behavior of alkali beta-diketone compounds, is conjectured to be



A structure of this type would yield a quadridentate chelate, essentially neutral and extractable from aqueous into organic solvents. Crowther and Moore[31] added xylene to the nitromethane to serve as a diluent, to improve the mechanical properties, and to decrease the aqueous solubility of the nitromethane.

The sharp increase in extractability with the use of lithium and nitromethane is not so surprising when one notes that Hasted, Ritson, and Collie[32] have observed a marked decrease in the dielectric constant of water with even small quantities of Li^+ added (the dielectric constant of LiCl aqueous solutions at 25°C is 71 at 0.5M, 64 at 1.0M, and 51 at 2.0M as compared to the normal dielectric constant of water at 78.5). Since the nitromethane dissolved in the aqueous solution would further lower the dielectric constant, it can be presumed that the dielectric constant of the aqueous phase would approach that of the organic under the conditions fixed by Crowther and Moore. The discussion given by Lee[33] can also be of value in understanding the effect of electrolytes on the dielectric constant of solvents and the corollary effect on the activity coefficients of individual ions.

Consideration of the various factors indicates: maximum extraction is attained at pH 8.7 but that a pH of 9 should not be exceeded because of the danger of TTA decomposition; above a lithium concentration of 0.02M in the aqueous phase, no further improvement of cesium extraction is achieved; and a 0.5M concentration of 1 : 1 nitromethane–xylene is optimum. Some Na^+ is extracted along with the Cs^+.

The selectivity of the procedure for cesium can be improved by the addition of highly water-soluble complexing agents to the aqueous phase to prevent extraction of unwanted ions. Ethylenediaminetetraacetic acid forms complexes efficiently with many metal ions at a pH of 8 and above. Other complex formers — citrate, tartrate, oxalate — could also be used.

Safety Consideration of Organic Solvents

Although chemists, by reason of their training, are considered to be technically proficient and thus to be well aware of the working hazards of both radioactivity and organic solvents, both nitromethane and nitrobenzene present unusual hazards that should be noted by chemists working with either for the first time. For nitromethane, according to the American Industrial Hygiene Association,[34] a maximum atmospheric concentration of 100 ppm by volume should not be exceeded in an 8-hr day. The fire and explosion hazard is rated as moderate. The shock stability is good, but the shock sensitivity can be increased by the addition of aniline, ethylenediamine, and similar alkaline compounds.

Mixtures of undiluted nitromethane with amines and heavy metal oxides are very hazardous because of the formation of fulminates. Nitromethane and dry or highly concentrated alkalies form salts that decompose explosively if heated or subjected to shock in the dry state. Nitrolic acids are formed when nitromethane reacts with nitrous acid, and salts of these acids are explosive when dry. Caution is advised when trying out new mixtures or reactions with nitromethane until the safety of the reaction has been established. Equipment should be designed to avoid sud-

den and adiabatic compression, and detonation traps should be installed on both sides of a pump handling nitromethane.

With nitrobenzene[35] the chief hazard appears to be its toxicity. The recommended maximum atmospheric concentration for 8 hr is only 1 ppm by volume of air. Up to 200 ppm may be inhaled for 1 hr without serious disturbance, but the results are apt to be almost immediately fatal if significant areas of the body are in contact with the liquid or if clothing is saturated with the liquid. Inhalation of massive concentrations may likewise prove to be quickly fatal.

Correlation of Principles and Specific Systems

Slater's guidelines follow closely the observed behavior of cesium with many extractants. Logically, an extractant system could be developed for cesium by combining it with almost any large, weakly charged anion and, at an optimum *p*H, extracting the ion-pair combination into a high-dielectric organic medium. Almost all the systems previously cited follow this pattern. The polyhalides are exceptional in that such extraction systems are operable at low *p*H, but the complexity of the halide systems involving shifts from the uncharged organic-soluble to the multiion singly charged species could account for the effective low-*p*H behavior of the system. The formation of strong acids of the type H_2MX_4 with the halides may also help to explain the strong acid extractions. The phenol, BAMBP, is considered to form a coordination complex rather than an ion-association pair with cesium.

The only other exception to Slater's predicted system is the TTA extraction of Crowther and Moore. The forcing of cesium into a pseudochelate structure with TTA and nitromethane by addition of Li^+ to the aqueous phase points up the fact that the chelate coordination compound is a creature of its environment. Since the fixed characteristics of the Cs^+ ion are unfavorable to chelate formation, the only other possibility is alteration of the solvating medium. Actually, Slater indicates the favorable effect of increasing the salt concentration or the organic solvent solubility of the solvating medium and attributes the improvement in extraction to the decrease in dielectric constant.

The choice of the organic solvent completes the picture of the extractive system. Although Crowther and Moore title their paper "The Extraction of Cesium with TTA," a glance at the postulated structure of the chelate shows that nitromethane is as much involved as is the TTA, since the quadridentate structure is bound equally to the oxygen of the nitromethane. In no sense can the solvent be regarded only as an "inert" medium as indeed it cannot in any solvent extraction system. In connection with Slater's work, the possibility is raised that not only is the high dielectric property of the nitromethane important, but also the coupling between the cesium and the oxygen atoms of the nitromethane is of consequence, as Crowther and Moore have indicated.

Although solvent extraction is not presently being used to reclaim cesium from nuclear fuel reprocessing wastes, process chemists still foresee applicability for the technique. The presently used inorganic ion-exchange process followed by the alum solid–liquid "extraction" offers the advantage of convenience in shipping and makes use of well-tried technology but will not preclude the adoption of a more sophisticated solvent extraction technique if a clear superiority can be demonstrated.

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The Chemistry of the Electromagnetically Separated Stable Isotopes

Abstract: The purification method is described for the stable isotopes of cerium electromagnetically enriched at Oak Ridge National Laboratory. The cerium oxide residue from the ignition of graphite pockets is dissolved in a mixture of HNO_3 and H_2O_2, precipitated as $Ce(OH)_4$ with ammonium hydroxide, and ignited to CeO_2. The CeO_2 is dissolved as before, precipitated as the oxalate, and ignited to CeO_2, the inventory form.

This is the third article of a series[1,2] on the chemistry of electromagnetically separated stable isotopes enriched at Oak Ridge National Laboratory. The general problems and methods associated with the handling and purification of isotopically enriched materials and with their chemical and isotopic anal-

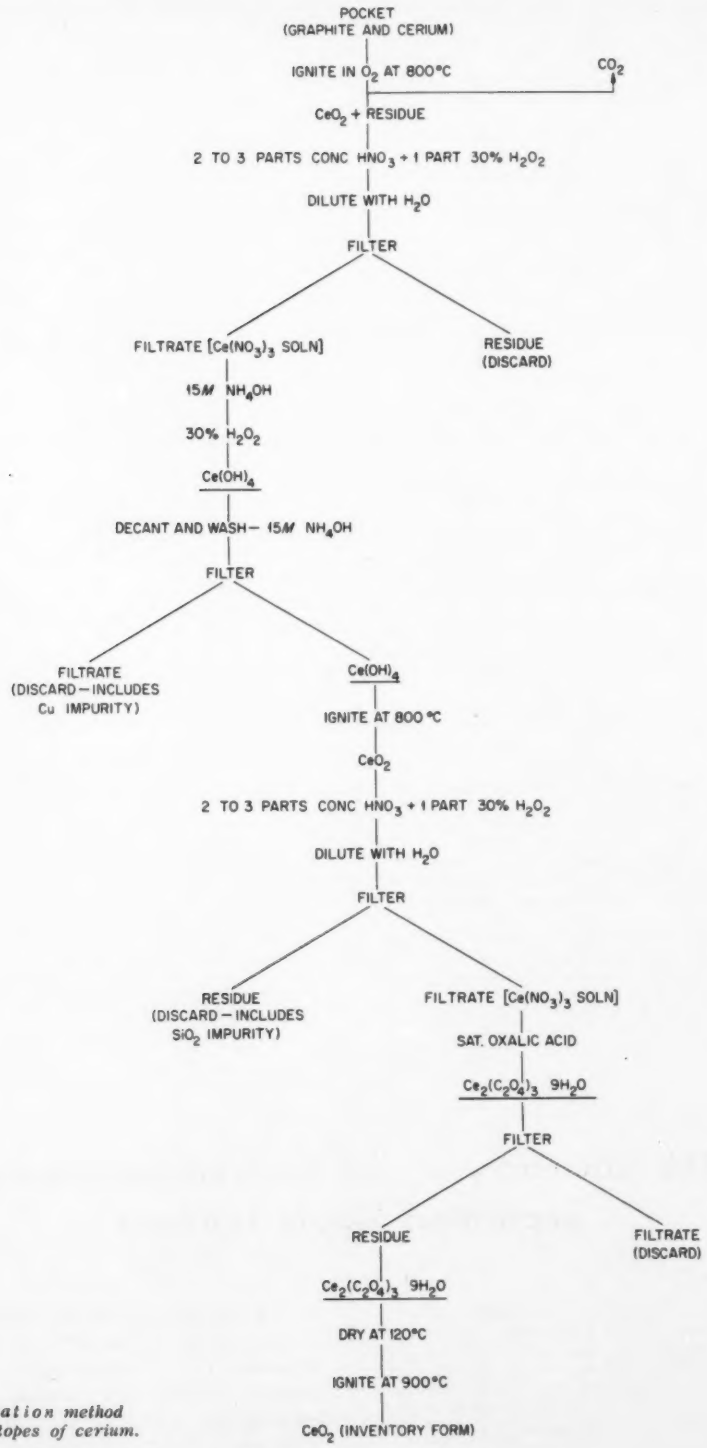

Fig. 1 Purification method for enriched isotopes of cerium.

ysis were described in the first article of the series, which also included the chemical processing methods for the enriched isotopes of Sr, Ba, Pb, Zr, and Hf. In the second of the series the processing methods for Cr, Pt, and Os isotopes were given. In this issue the chemical processing of enriched isotopes of cerium is described.

CERIUM

Cerium has four naturally occurring isotopes; three are stable and one, ^{142}Ce, is very slightly unstable (alpha-particle emission), with a half-life of 5×10^{15} years. The method (Fig. 1) for the chemical processing and recovery of separated cerium isotopes is relatively simple, involving only a double precipitation—first as the hydroxide and then as the oxalate—with subsequent ignition to CeO_2.

The most recent separation of cerium isotopes, Series MX (Ref. 3), provided >1100 g of recovered isotopes with isotopic abundances as follows:

Isotope	Isotopic abundance, at. %	
	Natural	Enriched
^{136}Ce	0.193	35.38
^{138}Ce	0.250	14.32
^{140}Ce	88.48	99.70
^{142}Ce*	11.07	92.77

*Slightly unstable, half-life 5×10^{15} years.

Graphite pockets are used for collection of the cerium isotopes. After removal from the calutron, openings in the collector pocket are sealed with cellophane tape. The outer surfaces of the pocket are cleaned by buffing with Al_2O_3-coated abrasive cloth, and the thick, heavy ends of the pocket are removed to decrease both ignition time and quantity of impurities originating from the graphite. The tape covering the openings is then removed, and the pocket is crushed in a plastic bag or sheet.

The crushed graphite containing the isotope deposit is transferred to a quartz boat, and the boat and contents are ignited in oxygen at 800°C in a horizontal quartz or Vycor tube furnace. When the graphite has disappeared, the residue, mostly cerium oxide, is cooled, transferred to a beaker, and digested at room temperature in a mixture of 2 to 3 parts of concentrated HNO_3 and 1 part of 30% H_2O_2 until completely dissolved. Additional H_2O_2 may be required to promote dissolution, but, after all the cerium has dissolved as $Ce(NO_3)_3$,* any H_2O_2 remaining must be decomposed by heating on a steam bath. The solution is cooled, diluted with an equal volume of water, and filtered.

Ammonium hydroxide (~15*M*) is added to the filtrate until it is alkaline, and then 30% H_2O_2 is added drop by drop until all the Ce^{3+} is completely oxidized to Ce^{4+}. Again, excess H_2O_2 is removed by heating on the steam bath. The $Ce(OH)_4$ precipitate is allowed to settle, the supernatant liquid is decanted, and the precipitate is repeatedly washed with 15*M* NH_4OH until there is no evidence of the blue copper† complex. All the decanted solution and washings are filtered through the paper on which the precipitate is collected. The precipitate is further washed on the filter paper with 15*M* NH_4OH, and the residue, with the paper, is transferred to a Vycor dish and ignited to CeO_2 at 800°C.

The CeO_2 is dissolved as before in 2 to 3 parts of concentrated HNO_3 and 1 part of 30% H_2O_2, and excess H_2O_2 is removed by heating on the steam bath. The solution is cooled, diluted with an equal volume of water, and then filtered to remove any silica present.

Cerium is precipitated from the filtrate by adding saturated oxalic acid solution while stirring. The precipitate is digested on a steam bath, collected on filter paper, and washed with saturated oxalic acid solution. The oxalate precipitate and paper are transferred to a Vycor container and dried at 120°C in an oven. The cerium is converted to CeO_2, the inventory form, by ignition at 900°C. (R. E. Greene)

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*Cerium is in the lower valence state (i.e., 3^+) because H_2O_2 is a reducing agent in acid solution.

†Introduced by sputtering in the calutron (i.e., volatilization of copper from calutron components).

PRODUCTION OF HIGH-SPECIFIC-ACTIVITY ^{132}Cs

A method for producing ^{132}Cs of >99.9% radiochemical purity has been awarded patents in Japan (No. 49,349, Nov. 2, 1962) and Germany (No. 1,208,421, Jan. 5, 1966). The method consists in irradiating an organic or inorganic cesium compound with bremsstrahlung of at least 10 Mev, producing ^{132}Cs by the reaction $^{133}Cs(\gamma,n)^{132}Cs$. For example, 5 mc of ^{132}Cs with a specific activity higher than 1 mc/g was produced by a 10-hr irradiation of 1.47 g of cesium nitrate with 20-Mev bremsstrahlung. The bremsstrahlung was produced by a 30-μa electron beam from a linear accelerator. The inventors are K. Tanaka, T. Kuroyanagi, T. Tamura, and N. Shibata. (MG)

Section

II

Isotopes and Radiation Technology

Isotope Technology Development

Radio-Release in Review

By Joan E. Carden

Abstract: This article defines and discusses the development of the radio-release method of materials analysis. The Kryptonates are excluded, but 11 other successful radio-release techniques are discussed in detail, and sensitivity data are presented.

This article is a review of radio-release techniques* but excludes methods involving the Kryptonates,† which were recently covered in two consecutive issues of *Isotopes and Radiation Technology*,[1] and the unsuccessful attempts by Richter and Gillespie[2] to develop a radio-release procedure for the determination of calcium and phosphorus in fertilizer matrixes.

Analytical methods using radioactivity are divided into two broad categories — methods dependent upon radioactivity as a source of ionizing radiation and methods dependent upon the tracer characteristics of radioactive material.[3] The term *radio-release* was coined by Richter[4] of Research Triangle Institute to describe a tracer technique in which a sample is analyzed without the necessity of the radioactive isotope being embodied in the sample from the beginning of the experiment. It is a method in which a nonradioactive component is indirectly determined by the quantitative release of a radioactive material from a radioactive reagent with which the sample is contacted.[5]

In the early 1960's, Richter was searching for a sensitive method for the determination of oxygen in water. He felt that a method of analysis by radiochemical exchange in a gaseous medium — patented by Chleck and Ziegler of Tracerlab — should be applicable to an aqueous solution. The patent, filed in May 1957 by Chleck and Ziegler,[6] claimed "a method of detecting the presence within a [gaseous] medium of a predetermined [gaseous] nonradioactive compound capable of evolving a radioactive [gaseous] effluent from a reactive material containing a radioactive element comprising the steps of exposing said medium to said reactive material to provide a test substance, which includes said radioactive element in an effluent only when said predetermined compound is present in said medium, and sensing the radioactivity of said test substance." By virtue of this patent, Chleck and Ziegler are the inventors of the technique of radio-release, the generally accepted term for what Chleck and Ziegler call "radiochemical analysis by radiochemical exchange."[7] This patent, which relates to the determination of SO_2 by use of a radioactive chlorate, does involve a direct radiochemical exchange reaction; however, this is not the case for all radio-release techniques. The radio-release method has evolved to include direct radiochemical exchange reactions, indirect radiochemical exchange reactions, and release by physical change of state.[8]

The radio-release technique is based upon the selective reaction of the sought constituent with a radioactive reagent of suitable specific activity. During the reaction, activity is released as a gas or as a very easily separable chemical species. The amount of sought constituent can be calculated from the amount of activity released, the specific activity of the reagent, and the stoichiometry of the reaction.[9] This article does not include as radio-release such techniques as (1) a quantitative precipitation in which the radioactive element is "tied up" as a precipitate,[10] (2) a quantitative isotope-exchange method in which a radioactive isotope replaces, without a reaction, a stable isotope of the same element,[11] and (3) radiometric titrations.[12]

In 1963, four radio-release techniques were reviewed in *Isotopes and Radiation Technology*.[5] Today the number of published radio-release techniques is at least 12. Each of 11 radio-release techniques, in-

*We would like to thank H. G. Richter, Research Triangle Institute, Durham, N. C., and W. S. Lyon, ORNL Analytical Chemistry Division, for their time and contributions as reviewers.

†Trademark of Panametrics (formerly Parametrics), Inc., Waltham, Mass., for solid, radio-release reagent sources.

cluding 3 techniques for the determination of SO_2 and 2 for the determination of oxygen, is discussed in detail, and sensitivity data (the smallest concentration that can be determined) are presented.

Chlorine-36 Release in Determination of SO_2

The first radio-release work—on the determination of SO_2—apparently was done by Chleck and Ziegler[6,13] of Tracerlab, Inc., in 1957 (Ref. 14). Sulfur dioxide, a product of the combustion of sulfur-bearing coal, has been recognized for years as one of the more serious air pollutants. It is an irritant gas that affects the eyes and the mucous membranes of the nose, throat, and lungs.[15] The generally accepted maximum allowable concentration that can be tolerated for several hours without serious disturbance, or with but slight symptoms, is 10 ppm. Because of its toxicity, sulfur dioxide has probably been examined by more analytical techniques than any other single pollutant. By 1957, several types of instruments for monitoring SO_2 were available, but they were expensive and complicated.

Chleck and Ziegler set out to develop a simple, low-cost instrument capable of instantaneously and quantitatively indicating the presence of even trace amounts of SO_2 in air and suitable both for field studies of air pollution and for process control. In the Tracerlab instrument, air enters a prefilter (typically, powdered zinc to eliminate hydrochloric acid), which removes gases that may undesirably affect the analysis but selectively passes substantially all the sulfur dioxide to a reaction cell. In the reaction cell a radioactive chlorate ($^{36}ClO_3^-$) reacts with the sulfur dioxide to produce a radioactive gas, chlorine dioxide ($^{36}ClO_2$). The quantity of chlorine dioxide produced is directly related to the amount of sulfur dioxide entering the reaction cell. The reaction was thought especially advantageous for detecting minute quantities—0.33 to 33 ppm—of SO_2, since the efficiency was ~97%. Practically, the reaction was disadvantageous: the specific activity of the chlorine was too low, and the chlorine dioxide reacted with the cell walls and contaminated them.[14]

Iodine-131 Release in Determination of SO_2

A radio-release method developed by H. H. Ross and Lyon[9] of Oak Ridge National Laboratory (ORNL) for the determination of SO_2 is based on the release of radioactive iodine according to the reaction:

$$5SO_2 + 2K^{131}IO_3 + 4H_2O \rightarrow K_2SO_4 + 4H_2SO_4 + {}^{131}I_2$$

The reaction is carried out in solution by forcing air through a bubbler train containing an alkaline potassium iodate solution. After the sample has reacted, the solution is acidified, and the liberated iodine is extracted. The activity of the iodine extract is determined and the amount of sulfur dioxide calculated.

The method is characterized by extreme sensitivity and a wide range, i.e., sulfur dioxide can be determined from 8×10^{-4} to 0.2 ppm in a 100-liter sample. This range is not fixed, however, since the specific activity of the reagent can be varied over wide limits. The only potentially significant interfering substance is hydrogen sulfide, but this is not a real problem, since hydrogen sulfide levels in the atmosphere are typically lower than those of sulfur dioxide by more than two orders of magnitude.

Calcium-45 Release in Determination of Aluminum in Carbon Steel

In a study of trace elements in metals reported in 1959, Amano[16] of the Research Institute for Iron, Steel, and Other Metals (Japan) determined aluminum in carbon steel by the release of ^{45}Ca in the exchange of aluminum for the radioactive calcium. The steel sample is dissolved in 6*M* HCl and extracted with ether to remove the iron. Any remaining iron in the aqueous solution is reduced to Fe^{2+} with SO_2. The test solution is passed at a rate of ~2 ml/min through a cation-exchange-resin column in the ^{45}Ca form. The aluminum is exchanged stoichiometrically with the ^{45}Ca ion and is determined by measuring the radioactivity in the effluent. The results of the radio-release technique compare favorably with the results of the oxine-benzene extraction method. Of the potentially interfering ions, only the ammonium ion presents a problem and requires control.

Tantalum-182 Release in Fluoride Determination

Fluoridation of public water supplies, use of fluoride chemicals in industrial processes, and fluoride pollution control of waste streams and air have resulted in an increased interest in the determination of fluoride. Moore[17] of ORNL has developed a radio-release technique for the determination of fluoride which might find some applications because of its speed and selectivity. Tantalum-182, when added to a known volume of an acidified fluoride solution, can be extracted as a fluoride complex into an organic solvent, diisobutylketone. The amount of activity extracted and counted is proportional to the fluoride ion concentration; i.e., the ^{182}Ta released from the aqueous to the organic phase is a measure of fluoride concentration. The sensitivity is ~8 μg/ml. The counting rate varies linearly over the range 80 to 168 μg/ml; below 80 μg/ml the counting rate does not vary linearly but it is reproducible.

Tritium (^3H) Release in Determination of Active Hydrogen with Lithium Aluminum Tritide

One of the first highly publicized radio-release techniques was the determination of active hydrogen (easily exchangeable hydrogen) with lithium aluminum tritide as developed by Chleck et al.[18] Lithium aluminum tritide in diethyl carbitol was reacted with four typical labile-hydrogen-containing compounds — *n*-butanol, benzoic acid, aniline, and water — and the activity of the evolved tritium was counted; the counts are proportional to the amount of active hydrogen. With each compound a different specific activity was used, and linearity of response was obtained in the plot of each of the above compounds. The value of the method as an analytical tool is enhanced by the fact that it is not necessary to prepare a solution of a given or a known specific activity; however, the specific activity must be high enough to yield adequate counting rates.

The lithium aluminum tritide used in the study had a specific activity of 2.5 mc/mg and was diluted with lithium aluminum hydride by a factor of 10^5 to yield specific activities of 3 to 20×10^{-4} mc/mmole. The theoretical sensitivity with undiluted (2.5 mc/mg) lithium aluminum tritide would be of the order of 10^{-8} mmole of active-hydrogen compound. With lithium aluminum tritide of greater specific activity than 2.5 mc/mg, the sensitivity could be easily brought into the submicrogram range. For practical purposes the sensitivity attainable is limited only by the ingenuity of the analyst in devising more efficient techniques, such as a better system of injection for small sample volumes.

Iodine-131 Release in Dissolved-Oxygen Determination

A radioactive ^{131}I-release technique, devised by W. J. Ross[19] of ORNL, was intended to enhance both the sensitivity and the precision of the classical Winkler method, which is the method by which most dissolved-oxygen determinations are still being performed. Dissolved oxygen is of particular interest in the study and prevention of corrosion and in biological studies relating life processes to oxygen concentration.

In this modification of the Winkler method, radioactive ^{131}I is incorporated in the potassium iodide reagent, and the iodine formed by reaction with molecular oxygen is extracted into chloroform and measured by counting the emitted gamma activity. By extracting the iodine as soon as it is formed, potential errors caused by such oxidizing agents as nitrite and ferric ions are eliminated, as is the need for reducing or complexing agents. The sensitivity (4 μg/liter) exceeds those of the most exact visual colorimetric starch (80 μg/liter) or instrumental colorimetric starch (16 μg/liter) methods but is less than that of the amperometric method (0.2 to 0.6 μg/liter). Oxygen in concentrations of 19 μg/liter to 10 mg/liter can be determined with a precision of ±5% by using the appropriate concentration of potassium iodide.

Thallium-204 Release in Dissolved-Oxygen Determination

Since the radioactive ^{131}I-release method is strictly a laboratory method for the determination of dissolved oxygen, a definite need exists for an in situ determination of the dissolved-oxygen content in both fresh and seawater.

Two instrumental dissolved-oxygen determination techniques, neither of which has been wholly satisfactory, are:

1. The voltammetric reduction of dissolved oxygen at a platinum electrode as a measure of oxygen concentration. Not only does this oxygen analyzer have a tendency to drift, but it is temperature sensitive.
2. The rapid oxidation of thallium metal by an aqueous oxygen solution. The change in conductivity of the thallium-metal-column effluent stream compared with the conductivity of the influent stream is a measure of the oxygen concentration. One disadvantage of this technique is that the ions of other substances in the water diminish its sensitivity.

It occurred to Richter and Gillespie[20] and coworkers at Research Triangle Institute that, if radioactive thallium were incorporated into the thallium column, the effluent radioactivity would be a measure of the dissolved-oxygen concentration in the influent water and nonoxidizing ions would not interfere. The Research Triangle Institute analyzer, which is portable and battery-operated, consists of a 10-mm-diameter Teflon column containing a $Tl/^{204}Tl$ metal sponge below which is a flow-type G-M tube. Water containing the dissolved oxygen is introduced at the top of the column and allowed to flow slowly through it. Radioactive ^{204}Tl ions released by the reaction of dissolved oxygen with the thallium metal are detected by a G-M tube, the counting rate of the ^{204}Tl being a measure of the dissolved-oxygen concentration.

For pure water the ^{204}Tl (specific activity 2.04 mc/g Tl, to obtain good counting statistics) counting rate varies linearly with dissolved-oxygen concentration down to the lowest concentration investigated (0.1 ppm). At a higher specific activity, the precision (~±5% at the 1-ppm level) but not the sensitivity is improved. In sea and other salt waters, the ^{204}Tl counting rate, although reproducible, does not vary linearly with dissolved-oxygen concentrations above ~3 ppm because of chloride interference, and a calibration curve must be used. If the material were used at the specific activity received (4.48 curies/g ^{204}Tl),

the sensitivity of the method would approximate 0.1 ppm. The approximately ±5% precision at the 1-ppm level could be improved by using higher-specific-activity ^{204}Tl.

Silver-110 Release in Determination of Dichromate or Vanadate Ions in Natural Waters

Just as the ^{204}Tl radio-release technique was intended to supersede two less desirable instrumental techniques for determination of dissolved oxygen, so was the ^{110m}Ag-release technique intended by Richter and Gillespie[21,22] to replace the less sensitive colorimetric technique for determining the concentration of dichromate and vanadate ions when used as tracers to measure the volume flow rate of streams. Sodium dichromate or sodium metavanadate is discharged into the stream at a known rate, and water samples downstream are collected and assayed by pouring the samples through a radioactive-silver column. The ^{110m}Ag reacts with the dichromate or vanadate ion and releases a stoichiometric quantity of the ^{110m}Ag. Neither ^{60}Co nor ^{75}Se, the only other elements with suitable properties (cost, availability, half-life, radiations emitted, and behavior in the radio-release system) with dichromate and vanadate, was found to be satisfactory as a radioactive component of the system. The reaction between ^{60}Co and vanadate or dichromate requires a low *p*H, but acid dissolution of cobalt causes a serious background. Selenium-75 is oxidized only under the most severe oxidizing conditions, but vanadate and dichromate do not oxidize selenium rapidly even in 0.1*M* H_2SO_4, hence the choice of ^{110m}Ag, which undergoes the following reaction with dichromate ion and vanadate ion in acid solution:

$$Cr_2O_7^{2-} + 6^{110m}Ag + 14H^+ \rightarrow 6^{110m}Ag^+ + 2Cr^{3+} + 7H_2O$$

$$V(OH)_4^+ + 2H^+ + {}^{110m}Ag \rightarrow VO^{2+} + {}^{110m}Ag^+ + 3H_2O$$

The dichromate yields more silver per unit weight and is considerably cheaper than sodium metavanadate, but is toxic to lower life forms, such as plankton. The potential interfering ions—chloride and ferric—in unpolluted streams are reduced or eliminated by pretreatment of the water with reagents such as 1,3-diethyl-2-thiourea and phosphorous acid, respectively. The solution will contain ^{110m}Ag ions in direct proportion to the original concentration of the dichromate or vanadate ion. Counting the activity in a portion of the solution permits the concentration of the dichromate or vanadate to be determined. The technique is reproducible and the sensitivity in the vanadate determination is 0.1 ppm vanadate ion and in the dichromate determination is increased from a minimum of 1 ppm dichromate ion, conveniently measurable by the colorimetric method, to 0.03 ppm, measurable by the radio-release method.

Carbon-14 Release in Determination of Moisture in Gases

Chemical and nuclear engineers and the food-drying and -freezing industries are among those interested in the determination and continuous monitoring of small amounts of moisture in gases and vapors. Previous methods seem predisposed to disadvantages such as limited sensitivities and numerous interferences. A radio-release technique in which water reacts with a labeled reagent, e.g., ^{14}C-labeled carbide, to yield a radioactive gas such as acetylene was conceived by Richter and Gillespie[23] and investigated and developed as a practical method by Houtman and Medema.[24]

A serious problem in this technique has been the preparation of the labeled carbides. The reactions suitable for their preparation,

$$CaO + 3C \xrightarrow{3000°C} CaC_2 + CO$$

$$2BaCO_3 + 5Ca \xrightarrow{1500-2000°C} CaC_2 + 2BaO + 4CaO$$

$$2BaCO_3 + 5Ba \xrightarrow{1500-2000°C} BaC_2 + 6BaO$$

$$2BaCO_3 + 5Mg \xrightarrow{700°C} BaC_2 + BaO + 5MgO$$

do not necessarily produce pure carbides, since there may be impurities from the starting materials and, in the case of the last three reactions, large amounts of oxides. Therefore differences in reaction rates and in the amount of radioactive acetylene produced per molecule of water are observed in carbides prepared by different reactions and from different batches.

The reaction of water with carbides to produce acetylene can proceed with the formation of oxides (BaO, CaO) or corresponding hydroxides, depending upon the vapor pressure of the water in the gas; the oxides or hydroxides can be interconverted or converted into hydrates if the moisture content of the gas is being changed. Also, varying amounts of water may be adsorbed on the surface of any of the components present. Further, the formation of oxides, hydroxides, and hydrates and the adsorption of water can be influenced by variation in temperature. Maximum sensitivity and the required linearity and response time are attainable with any of the available carbide mixtures by adjusting the temperature of, and the flow characteristics in, the carbide bed.

Figure 1 is a schematic diagram of the calibration apparatus and the apparatus used in the determination of moisture in gas. In the calibration apparatus a stream of nitrogen is first wetted with excess water vapor and then cooled to a known temperature. The gas then passes through the carbide bed (carbide powder, 0.25- to 0.50-mm diameter, mixed 1 : 1 with

porcelain beads of comparable size) of the analyzer and is led through a sampling valve to the shielded G-M detector (covered with 1 mg/cm^2 Mylar foil to prevent adsorption of acetylene by the detector cement) and to the flowmeter. A carbide mixture with a specific activity of 6 mc/g permits measurement of a moisture content as low as 1 to 10 ppm.

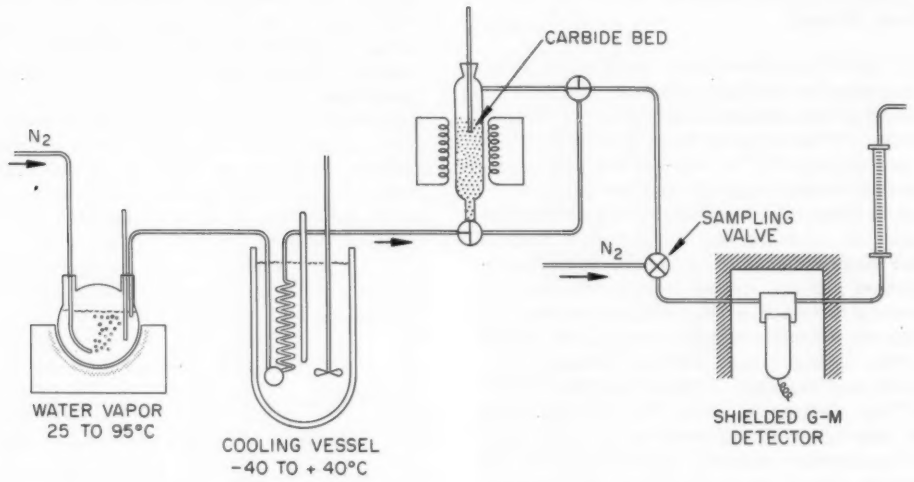

Fig. 1 Calibration apparatus and analyzer for the determination of moisture in gases.

Krypton-85 Clathrates

The "clathrates" (from Greek *klethra* and Latin *clathri* for "lattice") are a group of inclusion-type compounds, discovered by Powell,[25] in which a molecule of one substance is enclosed within a crystalline structure or "cage" by molecules of a second substance.[26,27] Powell prepared his nonradioactive inert-gas clathrates by heating a saturated aqueous solution of hydroquinone* (quinol) to 90°C and then slowly cooling (over a period of ~24 hr) the hydroquinone solution to room temperature in contact with an inert gas—argon, krypton, or xenon—at a pressure of ~40 atm. The product, a stable crystalline substance in which molecules of the gas are trapped in the hydroquinone crystal (Fig. 2), is filtered off, dried, and measured. The purpose of the high pressure is to provide a sufficient quantity of gas in solution so that atoms of gas will be available at the crystal-forming sites. The slow cooling rate allows equilibrium to be reestablished after any local depletion due to crystal formation.

Powell's technique was satisfactory for stable inert-gas clathrates. But preparation of similar radioactive clathrates by his procedure presented the problems of filtration of radioactive material, separation of radioactive aqueous solutions, and introduction of water vapor into the expensive radioactive gas.

A new class of krypton "compounds," which overcome the ^{85}Kr disadvantage of being difficult to use because of its lack of chemical reactivity and thus provide a useful source of beta radiation, was realized by the development, by Chleck and coworkers, of radioactive clathrates.[27–29]

Chleck and coworkers' initial radioactive clathrate preparation technique (which is simpler than Powell's, requires no filtering or drying, and eliminates water vapor) involves clathrate growth from a melt rather than from an aqueous solution. A 0.5- to 1.0-g sample of solid hydroquinone is put in a pressure bomb, atmospheric gases are eliminated, and the bomb is pressurized with krypton gas containing 5% ^{85}Kr. The pressure bomb is heated to 185°C to melt the hydroquinone and held there for 2 hr to allow the krypton to saturate the melt. The system is slowly cooled to room temperature over a long period of time. The bomb is opened, the fused sample (Fig. 3) removed, and the specific activity measured. The mass grown from a melt can be powdered into grains the size of salt or sugar. Although the grinding process deadens a portion of the reaction sites and results in a loss of gas at the reaction centers due to the high-temperature oxidations effected at the grinding points,[30] the

*Hydroquinone fulfills two of the most important requirements for the formation of clathrate compounds—an open crystal structure, with linkages that hold the molecule and crystal together and provide a rigid structure and a cavity of sufficient size, and small access openings to the enclosed cavity. Mock et al.[26] studied a number of other crystals but found none to be as good as hydroquinone.

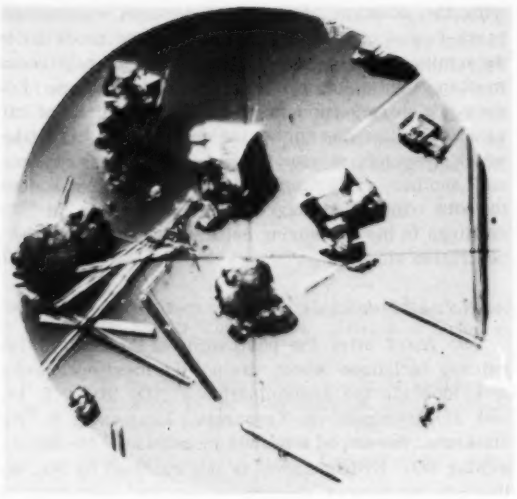

Fig. 2 A mixture of large rhombohedra of argon–hydroquinone clathrate in the beta-crystal form and needles of unclathrated hydroquinone in the alpha-crystal form. Magnification 40×. (Photomicrograph courtesy of H. M. Powell, Oxford University, Oxford, England.)

melt is still preferable to the powder or fine crystal grown from a saturated water solution.

As in Powell's procedure, high pressures and slow cooling rates give greater clathrate yields. Maximum clathrating efficiency,* 28.3%, was obtained at 60 atm and a cooling period of 72 hr. A maximum specific activity of 3.0 curies of ^{85}Kr (available as krypton gas containing 5% $^{85}Kr/g$)† hydroquinone has been achieved.[29] No appreciable effects of degradation due to the presence of internal radiation have been observed, and leakage from the cage is extremely small—a few parts per million per day.

In a patent filed in 1962, 3 years after the first radioactive clathrate papers were published, Chleck[30] discusses a new clathrating process in which hydroquinone is absorbed into a calcium silicate catalyst to give not only a finely dispersed powder but also a highly efficient reaction substance for ozone detectors. Approximately equal volumes of calcium silicate and hydroquinone are placed in an inert heavy liquid such as carbon tetrachloride. The calcium silicate settles to the bottom while the hydroquinone floats on top. The mixture is heated at the boiling point of the carbon tetrachloride; upon complete disappearance of the carbon tetrachloride, the mixture is poured off and dried. The resulting powder is placed in a pressure vessel and clathrates are prepared according to the Chleck et al. technique described above. These catalyzed clathrates display excellent stability over long periods of storage and have specific activities of up to 1 curie/g.

The clathrates are remarkably stable and can be oxidized only by very strong oxidants to release ^{85}Kr, which is trapped in a purely physical manner. The application of clathrates to chemical analyses capitalizes on the use of a radioactive material for measuring a nonradioactive chemical substance. The quantity of radioisotope released is proportional to the amount of incoming substance so that the detection and measurement of the activity also serve to determine the quantity of nonradioactive species entering the system. Applications of the clathrates include the determination of ozone and SO_2.

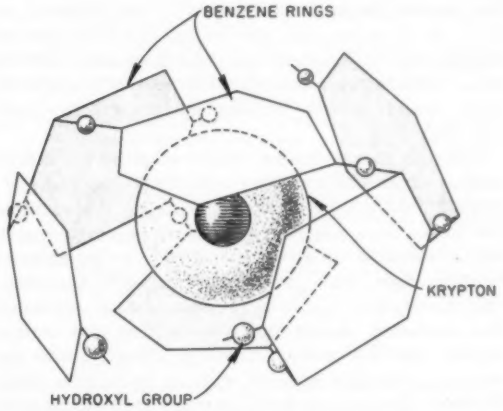

Fig. 3 Krypton-85 clathrate "cage"—an atom of ^{85}Kr trapped in a trimer of β-hydroquinone $[C_6H_4(OH)_2]_3 \cdot {}^{85}Kr$—resulting from recrystallization of α-hydroquinone under a positive pressure of krypton gas containing ^{85}Kr.

ANALYZER FOR OZONE

Ozone, a powerful oxidizing agent, is used industrially for bleaching fats, oils, waxes, flour, and starch and for the sterilization of drinking water. Ozone is very poisonous and has received considerable attention as an air pollutant. Concentrations >1 ppm, the generally recognized maximum permissible safe working concentration, have an irritating action on the mucous membranes of the respiratory system.[31] Because ozone is a component of the upper atmosphere, it has also attracted interest. For example, atmospheric studies have included the measurement of ozone in the upper troposphere and lower stratosphere to provide information on circulation in the atmosphere[32] and to show a close correlation between ozone concentration and radioactive fallout.[33]

In 1959 Chleck and Ziegler[28,34] undertook the development of a balloon-borne instrument for deter-

*The amount of gas trapped compared to the theoretical amount possible; i.e., the fraction of available cages that contain ^{85}Kr atoms.

†Krypton gas containing 5% ^{85}Kr is the most concentrated supply of ^{85}Kr now available and listed in the Oak Ridge National Laboratory catalog.

mining ozone for weather studies in the upper atmosphere. Since ozone is a strong oxidant, it will react with the hydroquinone of a clathrate to release the entrapped ^{85}Kr:

$$[C_6H_4(OH)_2]_3 \cdot {}^{85}Kr + O_3 \rightarrow 3C_6H_4O_2 + 3H_2O + {}^{85}Kr$$

The use of a clathrate provides not only high sensitivity but also allows construction of an analyzer of small size, low weight, and low cost.

The experimental ozone sensor, which consists of a clathrate source, a twin Geiger-tube measuring-cell arrangement, and a small air pump, is housed in the clear plastic case on top of a normal weather radiosonde. The pulse output of the Geiger tube is fed directly into the radiosonde transmitter, and the count rates are recorded on the ground by suitable rate-meter radio circuitry. The lower sensitivity limit (the count rate that is approximately equal to the normal background present in the system) of 10^{-10} g of ozone per liter of air (0.1 ppb) was obtained with a clathrate cell whose specific activity was ~100 mc/g. Higher-specific-activity clathrate cells would provide correspondingly greater sensitivities.

Although the apparatus described above for determining ozone has a greater sensitivity than that previously feasible by standard methods, the reaction for ozone is incomplete and yields only a few percent of what is theoretically possible on the basis of the high flow rates used for atmospheric sampling. The incomplete reaction is explained by assuming that oxidation occurs through reaction with atomic oxygen and not through reaction directly with the various molecular species such as O_2 and O_3. Thus the ozone in a gas stream undergoes slow equilibrium decomposition to atomic oxygen before reacting with the hydroquinone of the clathrate.

In 1962, Chleck[30] developed his second analyzer, using the highly efficient reaction substance produced by his improved process of clathrates with hydroquinone absorbed in calcium silicate. In this analyzer gaseous ^{85}Kr, which is released in an amount proportional to the ozone concentration in the gas stream, is swept into an air stream and then transported to a measuring cell that contains a G-M tube. The air stream is removed from the system by a pump that establishes the flow through the complete system. The signal output is flow-rate independent and varies only in response to ozone concentration, in contrast to most standard gas-analyzing systems with an output signal that is a function not only of reactant gas concentration but also of its arrival rate. Although ^{85}Kr is emitted as a function of the total ozone flux, the counting time is a function of the flow rate and compensates for variations in the flow rate—e.g., fast speed of gas flow, short counting time; slow speed of gas flow, long counting time.

Not only is the analyzer independent of flow rate and highly efficient with respect to the reaction (100% with the addition of a second catalyst—platinum-black-coated sand), but it can also be modified to determine the ozone concentration in a gaseous medium containing ozone and atomic oxygen. For such a determination the apparatus consists of two reaction cells: one containing an untreated clathrate, which responds to atomic oxygen in the gas stream, and another containing a clathrate, which responds to both ozone and oxygen. The difference in ^{85}Kr readings in the measuring cells shows the ozone concentration alone.

ANALYZER FOR SO_2

Two years after the publication of the first radio-release technique [which was not the most successful technique for the determination of SO_2 (Refs. 6, 13, and 35)] workers at Tracerlab, Inc., using a ^{85}Kr clathrate, developed a second instrument[36] for determining SO_2. Hydroquinone is not oxidized by SO_2, so the SO_2 is passed through a system consisting of $NaClO_2$ and ^{85}Kr clathrate in series, with the result that ^{85}Kr is released from the clathrate in an amount which is proportional to the SO_2 introduced. Small amounts of SO_2—as low as 0.05 ppm—have been detected.

Clathrates have been coupled with various reaction cells to provide an instrument, the Tracerlab Toxic Gas Monitor (Fig. 4), which has been designed to

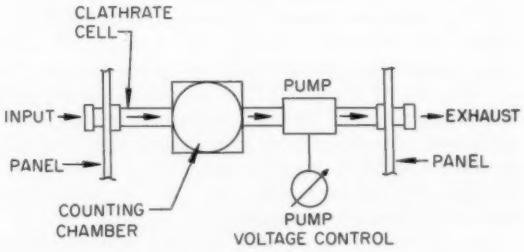

Fig. 4 Gas-monitor flow system.

detect and measure certain reactive gases—F_2, NO, Cl_2, and NO_2, as well as SO_2 and O_3—in the parts per million range. Completely separate instruments are used for the various gases; experience has shown that a multigas system has much poorer operational characteristics than the single-gas units.

Conclusion

We have defined radio-release and have included those techniques that "fit" our definition. Some of the techniques have already found considerable application because of sensitivity, speed, or instrument portability. Other techniques have not yet been applied; however, application of a technique should not

be the only measure of its value since tomorrow's needs for analytical techniques can never be anticipated. Mass spectrometry, which is used for analysis of process streams for impurities and for leak detection in the gaseous diffusion process, was developed by F. W. Aston in 1920 but was used purely as a research tool and not as a practical analytical tool until 1943.

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Asterisks indicate sponsorship in whole or in part by the U. S. Atomic Energy Commission, Division of Isotopes Development.

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RADIOMETRIC TITRATIONS

By T. Braun and J. Tölgyessy
(Translated into English by I. Finály and edited by A. Townshend),
168 plus vii pages, Pergamon Press, New York, 1967, $8.50

This book summarizes some 165 publications, mostly European, on radiometric titration. The subject is discussed according to the main type of chemical reaction involved—precipitate formation, complex formation, and redox reactions—and 41 elements that have been determined by such a method are tabulated according to the basic reaction. A number of reviews of this subject are cited, including one by the authors published in 1964. The authors emphasize that radiometric titration is useful as an analytical method but that overoptimism with regard to its potentialities would be detrimental to the further development of the technique. (MG)

Application of Radioisotopes for Surface-Area and Roughness Measurements

By Joseph Kivel*

Abstract: Radioisotope techniques for determining surface areas and roughness are reviewed. The techniques involve the formation of a monolayer of a labeled reagent on the surface to be measured and subsequent counting. The use of various labeled organic reagents, including surfactants, is described, and surface-area values obtained by the radioisotope method are compared with those obtained by the Brunauer, Emmett, and Teller (B.E.T.) method.

Surface area and surface roughness directly influence most physical and chemical phenomenons. Knowledge of surface characteristics has been shown to be significant to an understanding of such diverse phenomenons as radiation of heat, frictional drag, capacitance, rate of adsorption, dissolution rate, catalytic properties, and adhesion. If the degree of roughness of a material could be accurately measured, many properties could be predicted. As a result, a con-

*Atlantic Research Corporation, Alexandria, Va.

siderable effort has been expended to determine surface areas.

Initial studies to determine surface areas were based on gas adsorption. Langmuir,[1] in 1918, discovered that certain gases are adsorbed on a surface as monomolecular layers. By measurement of the gas pressure drop in a closed system due to adsorption by the surface, and with a knowledge of the surface area covered per molecule, the surface area of powdered materials could be determined. This technique gave highly reproducible surface-area values but was limited, because of its low sensitivity, to large areas and was not applicable when multilayer adsorption occurred.

Brunauer, Emmett, and Teller[2] expanded Langmuir's work both theoretically and experimentally in order to account for multilayer formation and for adsorption of polyatomic molecules. The technique developed by them, commonly known as the B.E.T. method, has become the "standard" for surface-area measurements. However, this method is limited to samples of large surface area—i.e., highly porous or powdered—and equipment calibration and measurement can be quite tedious.

Adsorption from solution has also been used to determine the surface roughness of a variety of materials. Adsorption from solution is similar to gas adsorption since, under certain conditions, a monolayer is deposited on a surface, and areas can be calculated if the molecular size is known. Most of these efforts have centered around the pioneer work of Langmuir and coworkers on adsorption of monolayers of fatty acids (in particular, stearic and oleic) on surfaces.[3]

Many other approaches to area determinations have been attempted. An excellent review of these techniques has been presented by Testerman.[4] Microwave, ion, electron, and light microscopy have all been attempted, but various disadvantages, e.g., poor resolution, uncertainty of proper function, and extremely high costs, have discouraged the use of microscopy.

Capacitance measurements have been used to determine surface areas of several metals. The use of these measurements to obtain roughness factors* has been investigated primarily by Hackerman[5] and by Testerman.[6] In this technique an electrolytic capacitor is assembled, with the surface to be determined acting as one plate of a condenser and ions in solution acting as the other. Since the layer of ions in solution will approximate the contour of the metal surface, the capacitance should be a measure of surface roughness. For metals the surface roughness is evaluated by comparison with a mercury surface assumed to be ideally smooth. This approach to surface-roughness measurement has been shown[6] to be useful for measurement of copper, steel, titanium, and pretreated aluminum surfaces.

*Roughness factor is defined as the ratio of the measured or true surface area to the calculated geometric area.

Radioisotope Techniques

As early as 1922, Paneth[7] used isotopes to measure surface areas. Finely powdered lead sulfate was shaken with a solution containing radioactive thorium-B (^{212}Pb) until equilibrium was reached. Only the surface atoms underwent exchange, and at equilibrium the ratio of lead to thorium-B in solution was equal to that on the surface of the powder. From a knowledge of the dimensions of the lead sulfate molecule and the activity on the surface, the surface area was calculated. The same method has been extended to other insoluble lead salts and to insoluble salts of other elements, notably the Group IIA (barium, strontium, calcium) sulfates.

This surface-exchange principle has been demonstrated with other isotopes. Marshall[8] studied chromium surfaces by adsorbing radioactive sodium from a sodium chloride solution. The surface area of iron has been determined[9] with ^{35}S. A method specific for the determination of the surface area of aluminum has been developed[10] which uses either radioactive chromium or phosphorus.

A considerable effort has been expended on gas-adsorption techniques using radioisotopes, usually of inert gases. The use of radioactive krypton[11] for surface-area determinations has been attempted, and the adsorption of radon has been used to study the surface area of glass.[12] A recent publication[13] indicated that surface areas as small as 1.0 cm^2 can be measured to ±10% using ^{133}Xe with an inactive carrier. Limited surface-area determinations have also been made with noninert gases; for example, Testerman[14] successfully employed ^{131}I for this measurement.

The greatest application of radiochemical techniques to surface-area measurements has been in studies of adsorption from solution, in particular, adsorption of organic compounds. Beischer[15] and later Kordecki and Gandy[16] extended the sensitivity of Langmuir's stearic acid work by labeling the fatty acid with ^{14}C. Studies of surface films formed by adsorption of other labeled fatty acids have also been made. Smith and Fort,[17] using *n*-nonadecanoic acid, found that monomolecular layers were formed on "clean" surfaces of cobalt and indium; however, Smith and McGill[18] encountered difficulty in forming monolayers on aluminum and experienced no formation of layers on tin and copper. The extent of surface oxidation also was shown[17,19] to strongly influence the amount of adsorption coverage.

The basis of the fatty acid technique is that, when the film-covered surfaces are withdrawn from solution, the liquid recedes, leaving a dry surface made up of a closely packed monolayer of the organic compound oriented with the polar group on the surface

of the solid and the hydrocarbon chain perpendicular to the substrate. Such a monolayer should impart an oleophobic character to the surface. This has not always been found to be true. Only a low degree of oleophobic character was observed in many instances of fatty acid adsorption,[20–22] indicating that the monolayer was either incomplete or easily removable.

In the most recent studies, adsorption of surfactants from aqueous solutions has been used to determine roughness factors. Since most materials form a negatively charged surface in aqueous solution, cationic surfactants have been the choice of the investigators. Kivel and coworkers used hexadecyl-1-^{14}C trimethylammonium bromide to obtain surface areas of glass,[23] metals,[24] and organic materials[25] in both planar and powdered forms. Haberman and Castorina[26] used the similarly tagged stearyltrimethylammonium bromide to obtain surface areas on organic surfaces but, because of the limited solubility of this surfactant in water, had to switch to a mixed-solvent system. Since that time they have changed to the hexadecyl compound.[27] Greenland and Quirk[28] also claimed excellent results in determining both internal and external surface areas of clays using the surfactant *N*-cetylpyridinium bromide. These surfactant studies were highly promising — measurements can be accomplished rapidly, only microcurie quantities of activity are involved, and the process lends itself readily to automation. One such technique and its potential applications are presented below. This surfactant system involves the use of ^{14}C-labeled hexadecyltrimethylammonium bromide (HMAB), but similar results and applicability may be possible with other surfactant systems as well.

Area Determinations with Labeled Surfactant

In the determination of surface area (and roughness-factor values), two assumptions are made: (1) the surface is occupied by a closely packed, oriented monomolecular layer; and (2) the area occupied by each molecule is the same as that calculated from molecular dimensions or for fatty acids and related compounds, the same as that for a film of a fatty acid on an aqueous substrate. In practice, however, the latter assumption can be ignored if comparison values (e.g., B.E.T.) are available.

Experimentally,[23] a monolayer of ^{14}C-labeled HMAB is adsorbed from aqueous solution onto the surface of the material whose surface area or roughness is to be determined. A 25-ml volume of a typical solution might contain 5 μc of ^{14}C. If the material has a planar surface, it is slowly removed from solution and then counted. From the specific activity and surfactant molecular dimensions, the surface area and roughness can be read from a nomogram or rapidly calculated. The surface areas of powdered materials are obtained by determining the loss in activity from solution, attributing this value to adsorption by the powder, and applying specific activity and molecular dimensions.

Investigations have been made on many types of planar surfaces and powders. Adsorption isotherms on all inorganic surfaces tested were similar, exhibiting monolayer-concentration plateaus over identical concentration ranges. The isotherms obtained for a series of metallic thin films deposited on glass (Fig. 1) all have a monolayer plateau, terminating

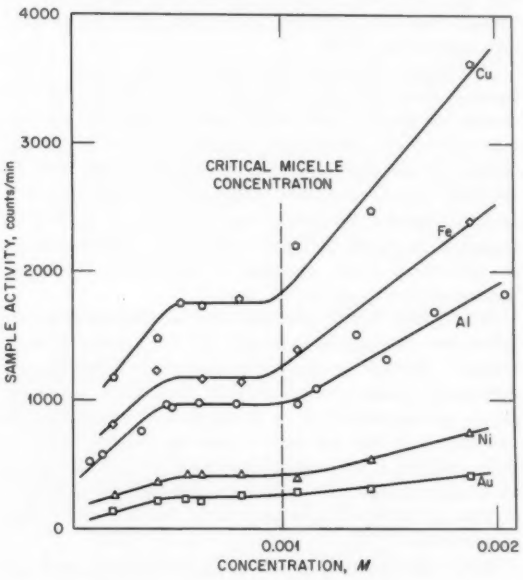

Fig. 1 HMAB adsorption isotherms on metals at 20°C.

at the critical micelle concentration (cmc), i.e., the concentration at which the long-chain cations begin to clump together to form aggregates. Adsorption isotherms for glass, silica, and titanium dioxide were similar.

A plateau in the adsorption isotherm indicates first degree saturation,[29] i.e., the condition at which all possible sites in the original surface are filled and further adsorption can take place only on new surfaces. For convenience, this degree of coverage may be called the formation of a complete "monolayer," but the layer may also contain solvent or consist only of isolated clusters of solute molecules adsorbed on the most active sites.

Further indication of monolayer formation by HMAB was obtained by Ter Minassian-Saraga[30] in a study of bromide adsorption on glass from HMAB solutions. The amount of bromide adsorbed on the glass was negligible until approximately the cmc was reached, at which point bromide adsorption increased rapidly

with increasing concentration (Fig. 2). It appears that, at concentrations below the cmc, only the HMAB cation is adsorbed on the glass surface. From the similarities of the adsorption isotherms on glass and on the metals investigated, it may be assumed that only cationic adsorption occurs below the cmc on metal surfaces as well. To preserve electrical neutrality of both the surface and the solution, cationic adsorption must be accompanied by substitution or exchange with cations adsorbed on the surface. Saraga postulated a "surface salt," i.e., $\equiv SiON(CH_3)_3C_{16}H_{33}$, obtained by replacement of the hydrogen of the hydroxyl group by the quaternary cation. Cationic adsorption onto metals can be interpreted by assuming substitution of the quaternary cation for the hydrogen of the adsorbed hydroxyl ion or water molecule.

Studies have been conducted on organic surfaces.[25] Although the HMAB adsorption isotherms for all inorganic surfaces were similar, those for two organic materials—cellulose diacetate and polytetrafluoroethylene—were identical to one another but were significantly different from those of the inorganic material. Adsorption isotherms for inorganic and organic surfaces are shown in Fig. 2. This was not surprising since the surfactant molecule does consist of a hydrophilic "head" and a long-chain hydrophobic "tail," and it is to be expected that such molecules would be adsorbed differently on polar and nonpolar surfaces. Several examples have been presented[29] of molecules that exhibit monofunctional adsorption leading to vertical close-packing on surfaces of the same polarity as the solvent or that "lie flat" and exhibit bifunctional adsorption on opposite polarity surfaces. This difference, as noted later, provides the basis for one set of potential applications.

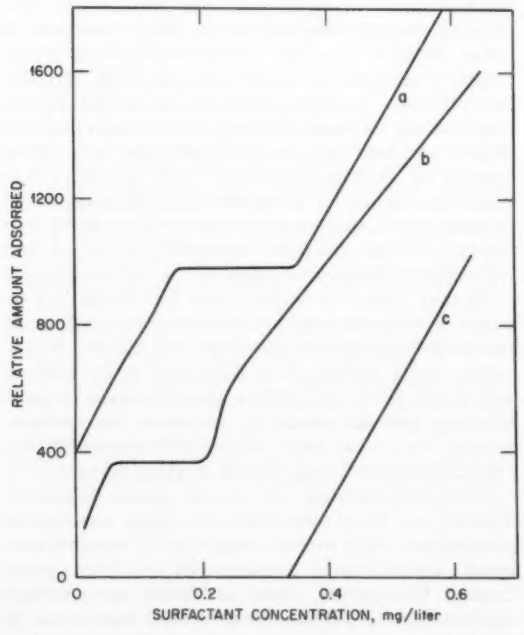

Fig. 2 Adsorption of surfactant (hexadecyltrimethylammonium bromide) on inorganic and organic surfaces. Hexadecyltrimethylammonium cation on (a) glass and (b) polytetrafluoroethylene; (c) bromide ion on glass.

For the determination of surface-area values, the area occupied per molecule and the specific activity of the adsorbed surfactant must be known. Comparisons with B.E.T. "standards" have shown that the value of 74.5 ± 2.5 square angstroms (A^2) must be used as the area occupied per molecule. The surface areas of TiO_2 and SiO_2 standards calculated using this value are:

Material	Surface area, m^2/g	
	HMAB method	B.E.T. method
TiO_2 standard	10.6 ± 0.4	10.3 ± 0.2
SiO_2 standard	24.4 ± 0.8	24.3 ± 0.6

The significance of these results is not in the agreement of the HMAB and B.E.T. values for each material but rather in the agreement between the ratios of surface-area values of TiO_2/SiO_2 obtained by the two different techniques. The closeness of the two ratios further indicates that the HMAB forms a monolayer on inorganic materials and that comparison between dissimilar materials is possible. The surface areas of organic materials have also been determined. However, B.E.T. comparison samples were not available. If the value of 74.5 A^2 is used for calculations of surface area of strips of polytetrafluoroethylene, an impossible roughness factor of less than unity results. This indicates either that adsorption is incomplete or, more likely, that the molecule is adsorbed horizontally, and thus the value of 74.5 A^2 for surface area covered per molecule is less than is actually the case.

Applicability of Surface-Roughness Measurements

Many physical, chemical, and electronic phenomenons depend directly on the treatment of the surface and the area of surface available to undergo the given interaction. Testerman[14] compiled several examples of such phenomenons:

1. Heat Radiation. In 1879 Stefan concluded, from measurements made by John Tyndall, that the heat emission rate of a body could be expressed by the relation $R = e\sigma T^4$, where R = rate of emission of radiant energy per unit area, e = emissivity of the surface, σ = constant of proportionality, and T = Kelvin temperature. The emissivity varies not only with the type of metallic surface but also with the treatment of the surface, i.e., it is larger for rough and smaller for smooth surfaces.[31]

2. Frictional Drag. The frictional drag imposed by one body on another depends on the type and roughness of the surfaces. The familiar frictional-force relation is $F = \mu N$, where F = frictional force, μ = coefficient of friction (dependent on the roughness of the material), and N = force normal to the surface. The relation between the surface roughness and coefficient of friction is essentially qualitative—few quantitative studies have been reported owing to difficulties in evaluating the surface roughness.

3. Capacitance. An ordinary capacitor is composed of two oppositely charged metallic plates separated by a dielectric. The capacitance of the condenser is a function of the available area as long as the two plates have matching contours. The capacitance is given by $C = \epsilon A/d$, where C = capacitance, ϵ = permittivity of the dielectric, A = area of plates, and d = distance of separation.

4. Adsorption Rate. Under ordinary conditions the gas-adsorption rate of metallic surfaces and catalysts depends on temperature, pressure, treatment of the adsorbent, and area available for interaction.

5. Polymeric Coatings. The polymeric coating of metallic surfaces depends on the surface conditions of the metal.[32] Consequently there is a critical need for a method to determine the degree of roughness of metallic surfaces. Since the surface characteristics of a solid depend on the history of the solid—its preparation, degree of purity, etc.—varying degrees of surface roughness are found in similar types of metals.

Several specific applications of HMAB are given below. Studies using HMAB have shown the effect of surface roughness on magnetic properties of thin permalloy films.[33] In one such experiment permalloy films from 1000 to 2000 A were deposited on thin glasses that had been roughened or polished by various techniques, and the magnetic properties of the films were determined. There was considerable variation in coercive force as the roughness factor of the substrate was changed (Fig. 3). A limiting value, dependent on film thickness, was reached at a roughness factor of approximately 25. In addition, as a result of this investigation, the phenomenon of biaxial anisotropy was observed for the first time in thin films; this may lead to new applications for these materials.[34]

Another study using HMAB has shown[22] that the surface roughness of thin films is affected by the environment. A humid or vacuum environment, and for some thin films an inert atmosphere, prevented roughening of these films. However, it was also demonstrated that certain magnetic films will roughen—and thus change magnetic properties—even in inert atmospheres. These studies have led to improved methods of storage for these films, and, although they were undertaken with magnetic films, the data generated have been applied to other thin-film systems and have been useful in certain corrosion studies.

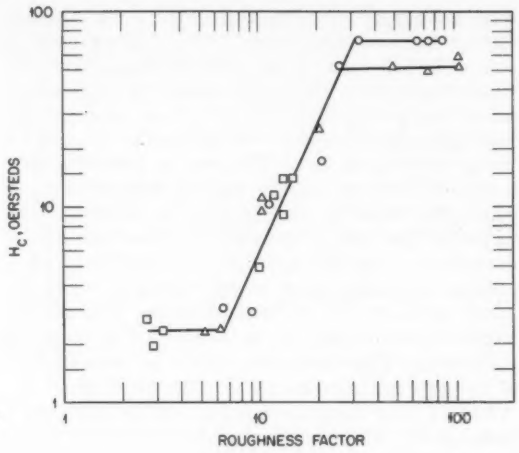

Fig. 3 Coercive force as a function of surface roughness (permalloy deposited on different glasses): ○, etched lead glass, film thickness 1000 A; △, etched lead glass, film thickness 1500 A; □, microscope cover glasses, film thickness 2000 A.

In addition to the published results described above, unpublished results using this surface-area-measurement technique have demonstrated the effect of variation of surface roughness on the flow of mercury on glass, which in turn has led to elucidation of a proprietary process for production of more reliable, low-tilt-angle mercury switches. In another unpublished study, localized "afterglow" on highly polished copper cathodes has been demonstrated to be due to regions of greater roughness. This discovery was made by taking an autoradiograph of a deposited monolayer of a labeled surfactant on the cathode. The location of the localized afterglow coincided with high-activity regions indicated by the autoradiograph.

Another group of applications for HMAB can be based on the difference in adsorption on organic and inorganic surfaces. In one study the amount of aluminum on the surface of an aluminum–epoxy mixture was determined; the surface area increased proportionately with the aluminum content of the mixture. Studies have also been attempted to determine the extent of organic contamination of glass surfaces.

These applications are by no means inclusive. Studies are being undertaken to relate rheological phenomenons with surface properties of selected material, and biological phenomenons are being investigated. Undoubtedly, there are many more isotope applications for surface-measurement techniques. In particular, since the amount of activity required is small (less than microcurie quantities are often used) and easily removable, these methods lend themselves to in-plant inspection techniques. (REG)

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RADIOISOTOPE MEASUREMENT APPLICATIONS IN ENGINEERING
By Robin P. Gardner and Ralph L. Ely, Jr.
Published by Reinhold Publishing Corporation, New York, 1967
xii + 483 pp.; 200 references

With the increasingly important role played by radioisotopes in American industry, textbooks are needed for teaching various aspects of their use. This one is intended for use in a two-semester lecture and laboratory course for training of engineers in the use of radioisotopes for measurement and control purposes. The scope is limited to applications of the effects of matter on radiation; effects of radiation on matter are excluded. The text covers, specifically, the use of radioactive tracers, gaging with alpha and beta particles, X and gamma rays, and neutrons; and radiography. Emphasis is on theory, and these subjects are discussed with considerable mathematical detail. Fifteen related laboratory experiments, which can be performed with simple, basic equipment estimated to cost about $5000 for a class of 16, are given. The usual background material—discussions and mathematics of radioactive decay processes, nuclear reactions, and interaction of radiation with matter—is presented in the first few chapters. Radiation-detection instrumentation, which is a significant feature of any radiation-application system, is discussed in detail, and radiation-safety principles and practices are described. The book was funded by the USAEC Division of Nuclear Education and Training and is clearly written and well edited. The student will find it a very useful companion volume to an earlier, more descriptive, text: *Radioisotope Applications Engineering* (Jerome Kohl, Rene D. Zentner, and Herbert R. Lukens, D. Van Nostrand Company, Inc., Princeton, N. J., 1961). (Martha Gerrard)

Availability of Standards for Common Radionuclides

By S. A. Reynolds*

Abstract: Radionuclides for which standard preparations are available or needed are listed in a table, together with some sources of supply. Some discussion of the use and importance of radionuclidic standards is included.

The availability of and requirements for radionuclide standards have been reviewed. Reliable standards are very important in the use of radionuclides, and the present article supplements information given in an earlier review,[1] which should be consulted for a general discussion and references. The present tabulation includes 93 nuclides which were considered. Of these, 35 have standards available from domestic suppliers and 35 others are available from foreign sources. Standards for 12 of the nuclides are indicated as being currently needed in the United States. The others included in the tabulation do not have confirmed requirements and may be adequately covered by substitute standards or detector calibration curves. Although the usefulness of some of the listed nuclidic standards should be obvious, the National Bureau of Standards (NBS) of the U. S. Department of Commerce has had very few inquiries about standards or calibration services.

*Oak Ridge National Laboratory, Oak Ridge, Tenn.

The 93 tabulated nuclides were taken from those listed by the National Academy of Sciences–National Research Council Subcommittee on the Use of Radioactivity Standards (B. Kahn), the Society for Nuclear Medicine (C. C. Harris), and others.[2,3] In addition, the table includes nuclides of significance in the environment according to reports of the U. S. Atomic Energy Commission (AEC) Health and Safety Laboratory (HASL), and nuclides for which methods have been published or are in preparation by the American Society for Testing and Materials Committees D-19 and E-10 and by the American Public Health Association. Many of the listed nuclides (Table 1) are included in the greatly enlarged version of the "Slack and Way Table"[4] now being prepared by the Oak Ridge National Laboratory's (ORNL) Nuclear Data Group. The half-life values listed in Table 1 are those used by ORNL, previously given in Ref. 5. These values may be updated as more accurate information becomes available. Because of the time needed for shipment, the listing in Table 1 is limited, with the exception of ^{99m}Tc, to nuclides of half-lives over 12 hr. In addition to the listed items, the International Atomic Energy Agency (IAEA) has supplied low-level standards in aqueous and environmental-type matrixes, for which inquiry should be directed

Table 1 AVAILABILITY OF RADIOACTIVITY STANDARDS, AUGUST 1967

Nuclide	Parent half-life	NBS* Std.†	NBS* Cal.‡	Nuclear-Chicago§	IAEA¶	RCC**	Need
^{3}H	12.3 years	X				X	
^{7}Be	53 days						
^{11}C	5730 years	X				X	
^{22}Na	2.6 years	X	X	X	X††	X	
^{24}Na	15.0 hr		X	X		X	
$^{28}Mg-^{28}Al$	21.3 hr, 2.3 min					X	
^{32}P	14.3 days		X	X		X	
^{33}P	25 days						
^{35}S	88 days		X	X		X	
^{36}Cl	3.08×10^{5} years	X	X	X		X	
^{42}K	12.46 hr		X	X		X	
^{45}Ca	165 days		X	X		X	
$^{47}Ca-^{47}Sc$	4.53 days, 3.4 days					X	X
^{46}Sc	84 days		X			X	
^{51}Cr	27.8 days					X	
^{52}Mn	5.7 days					X	
^{54}Mn	313 days	X††	X		X††	X	
^{55}Fe	2.7 years	X				X	
^{59}Fe	45 days		X	X		X	
^{57}Co	270 days		X	X	X††	X	
^{58}Co	71 days					X	
^{60}Co	5.26 years	X††	X	X	X	X	
^{63}Ni	~92 years					X	
^{64}Cu	12.8 hr					X	
^{65}Zn	245 days	X††	X	X		X	
^{69m}Zn	14 hr						
^{72}Ga	14.1 hr						
$^{68}Ge-^{68}Ga$	280 days, 68 min						X
^{71}As	18 days						X
^{76}As	26.4 hr					X	
^{75}Se	120 days					X	X
^{82}Br	35.4 hr					X	
^{85}Kr	10.7 years	X					
^{84}Rb	33 days						
^{86}Rb	18.7 days					X	
^{85}Sr	65 days		X			X	
^{89}Sr	51 days		X			X	
$^{90}Sr-^{90}Y$	28.6 years, 64.4 hr		X	X		X	
$^{87}Y-^{87}Sr$	80 hr, 2.8 hr						X
^{88}Y	107 days	X††	X		X††	X	
^{91}Y	59 days					X	
$^{95}Zr-^{95}Nb$	65 days, 35 days					X	
^{94}Nb	2.03×10^{4} years	X††					
^{95}Nb	35.0 days	X	X			X	
$^{99}Mo-^{99m}Tc$	66.7 hr, 6 hr					X	
^{99m}Tc‡‡	6.0 hr					X	X
^{103}Ru	39.7 days					X	
$^{106}Ru-^{106}Rh$	1.01 years, 30 sec					X	
^{110m}Ag	253 days					X	
^{111}Ag	7.5 days						
^{109}Cd	1.24 years					X	
$^{113}Sn-^{113}In$	118 days, 1.7 hr						X
^{124}Sb	60.2 days					X	
^{125}Sb	2.7 years					X	
$^{132}Te-^{132}I$	78 hr, 2.3 hr						X
^{123}I	13.0 hr						X
^{125}I	60 days	X				X	
^{129}I	1.6×10^{7} years						
^{130}I	12.5 hr						
^{131}I	8.06 days		X	X		X	
^{133}Xe	5.3 days						X
^{131}Cs	9.7 days					X	
^{134}Cs	2.07 years					X	

(Table continues on the next page.)

Table 1 (Continued)

Nuclide	Parent half-life	NBS* Std.†	NBS* Cal.‡	Nuclear-Chicago§	IAEA¶	RCC**	Need
$^{137}Cs-^{137}Ba$	30 years, 2.6 min	X††	X	X	X	X	
^{133}Ba	10.7 years					X	
$^{140}Ba-^{140}La$	12.8 days, 40.2 hr					X	
^{139}Ce	138 days	X††	X			X	
^{141}Ce	32.5 days	X	X			X	
$^{144}Ce-^{144}Pr$	284 days, 17 min	X				X	
^{147}Pm	2.62 years	X	X	X		X	
^{153}Gd	242 days						
^{170}Tm	129 days					X	
^{171}Tm	1.9 years						X
^{182}Ta	115 days			X		X	
^{192}Ir	74.0 days					X	
^{195}Au	183 days					X	
^{198}Au	2.70 days		X	X		X	
^{199}Au	3.15 days					X	
^{197}Hg	64 hr	X					
^{203}Hg	46.5 days	X	X		X††	X	
^{201}Tl	3.8 years		X	X		X	
$^{210}Pb-^{210}Bi$	21.3 years 5.0 days					X	
^{210}Po	138.4 days	X††				X	
^{226}Ra	1600 years	X	X			X	
$^{228}Ra-^{228}Ac$	5.7 years, 6.1 hr						
^{228}Th	1.91 years					X	
^{232}U	71.7 years						
^{239}Np	2.3 days						
^{239}Pu	2.44×10^4 years					X	
^{241}Pu	14.2 years						X
^{241}Am	433 years	X††			X	X	
^{242}Cm	163 days						
^{244}Cm	18.1 years						

*U. S. Department of Commerce, National Bureau of Standards, Washington, D. C. 20234.
†Std. = standard available.
‡Cal. = calibration service furnished.
§Nuclear-Chicago Corporation, 333 East Howard Avenue, Des Plaines, Ill. 60018.
¶International Atomic Energy Agency, Kärtner Ring 11, A-1010, Vienna 1, Austria.
**The Radiochemical Centre, Amersham, Buckinghamshire, England.
††Available only as a solid source.
‡‡Requires advanced scheduling.

to Analytical Quality Control Services, IAEA Headquarters.

Sources of standards (Table 1) are limited to some of the international and national organizations: NBS, the British Radiochemical Centre (RCC), and IAEA; one U. S. commercial organization, Nuclear-Chicago Corporation, is included, listing their preparations of which the stocks are routinely checked by NBS. The Oak Ridge National Laboratory, which still produces and distributes many radioisotopes, furnishes neither radionuclide standards nor calibrated solutions.*

Criterions for standards and their use were emphasized at a recent symposium.[8] Suppliers should furnish with each standard (or at least have available to answer inquiries) information on the form of the material, the method and accuracy of standardization, the properties assumed for the nuclide, and the radionuclidic purity of the preparation.[9,10] All of this information is essential to the conscientious user and may also help the supplier by pointing out possible shortcomings of his standard or unwarranted assumptions used in his calibrations. Although point sources on films or plates are sometimes satisfactory, provided that the samples are always prepared in an equivalent way, standards as solutions are unquestionably better. The user should recognize the importance of making calibrations with the nuclide that is to be measured, if possible, because corrections for efficiency variation, summing effects, etc., are sometimes difficult to apply. See, for example, the divergent results from a ^{197}Hg "round robin"[11] obtained by experienced and interested participants — manufacturers and users of the nuclide. If short-lived nuclides are used, the period between the calibrations may be extended if, at the same time that a

*Routine shipments from ORNL are not calibrated, and they should not be considered as standards. Analyses of these shipments are made by experienced people, using widely accepted methods and the best information available on properties of the nuclides. The overall precision of sampling, dilution, and analysis is from 2 to 10% (95% confidence level), and, taking into consideration the additional factor of absolute-measurement and decay-scheme uncertainties, the limit of error (mc/ml) is 3 to 30% (Refs. 6 and 7). Independent ORNL measurements of the activities of preparations furnished by standards organizations have shown very good agreement with the measurements by those organizations.

particular device (including source container, support, detector, and — sometimes — circuitry) is calibrated against a proper short-lived nuclide, the activity of a long-lived source of similar properties is also measured. The latter may then be used for subsequent normalization of data as the efficiency of the device changes with time. For example, ^{170}Tm or ^{204}Tl have been used as reference standards for ^{197}Hg, as has ^{57}Co for ^{99m}Tc.

Although standards can be obtained for some of the hundreds of nuclides encountered in radiochemical and isotope-applications work, more are needed. Hopefully, the necessary impetus to provide such standards will result from the recognition of their value by potential users. (FJM)

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11. J. S. Eldridge, Standardization of Mercury-197, in Ref. 8, pp. 313-322.

Radioisotopic Method for Measuring the Temperature of a Molten Metal*

Abstract: A method for determining the temperature of a molten metal from the intensity of the gamma radiation transmitted by it is described.

When the temperature of a molten metal is determined by a method that requires contact of the liquid phase with a foreign substance, impurities may be introduced into the melt. These impurities, in turn, may change the value of any physical constants of the fluid state which are being studied. A method was therefore developed, and is described here, for remote, continuous, contactless determination of liquid-metal temperatures.

The method is based on the principle that when a molten metal is heated its density decreases and, if a constant depth is maintained at the point of measurement, there is less attenuation of a beam of gamma radiation being transmitted through it. The intensity of the transmitted beam is a function of the temperature and may be used to measure the temperature of the metal in the liquid state.

For a molten metal of constant thickness d and a linear gamma absorption coefficient μ'', the intensity, I_t, of the gamma radiation transmitted at temperature t is related to that at the melting point, I_{t_m}, by

$$I_t = I_{t_m} \cdot e^{\Delta\mu'' d}$$

The intensity of transmission is measured at a few temperatures, which are known from standard temperature-measurement methods. From these values the term $e^{\Delta\mu''}$ is approximated by a straight line drawn through these few points, and the line is then extrapolated to higher liquid-phase temperatures. Thus a curve of intensity as a function of temperature (Fig. 1) is constructed for the molten metal under consideration. It is assumed that, to a first approximation, the transmission of gamma radiation by molten metals is independent of their aggregate state, i.e., the *mass* absorption coefficient of gamma radiation does not change with change in temperature of the transmitting metal.

The intensity of the transmitted gamma radiation is measured in a device (Fig. 2) that permits maintaining a constant thickness of molten metal in the region of measurement. As the volume of the metal increases with increasing temperature, the excess overflows into a restraining collar, thus keeping the thickness of the metal layer constant. The crucible and collar are fastened to a cooled base by holders in

*Based on an article, in Russian, by V. I. Kutovoi and V. I. Stetsenko in *Izmeritel'naya Tekhnika*, 1965, No. 8, pp. 17-20.

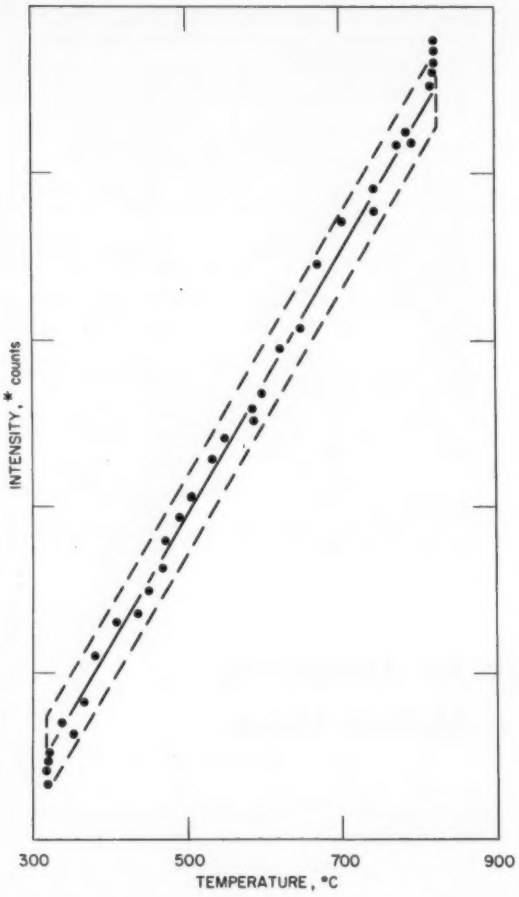

*Fig. 1 Increase in intensity of radiation transmitted by a 5.2-cm-thick layer of zinc (m.p. 419.5°C, b.p. 907°C) as the temperature is increased from about 300°C to about 850°C. *Exact values dependent on source intensity.*

such a way that a temperature change in the holders does not change the vertical distances. A water-cooled screen insulates the source and radiation detector.

Optimum thicknesses for several metals are listed in Table 1. The optimum source activity is determined from the basic equations for radioisotopic measurement of density.

In tests of the radioisotopic method for measuring molten-metal temperatures, the results were surprisingly close to those obtained with a platinum–rhodium/platinum thermocouple. Measurement errors were uniform and at temperatures around 2000°C were no more than 2%. The error can be minimized by selection of the proper source activity, electronics systems with minimum error, and optimum sample thickness.

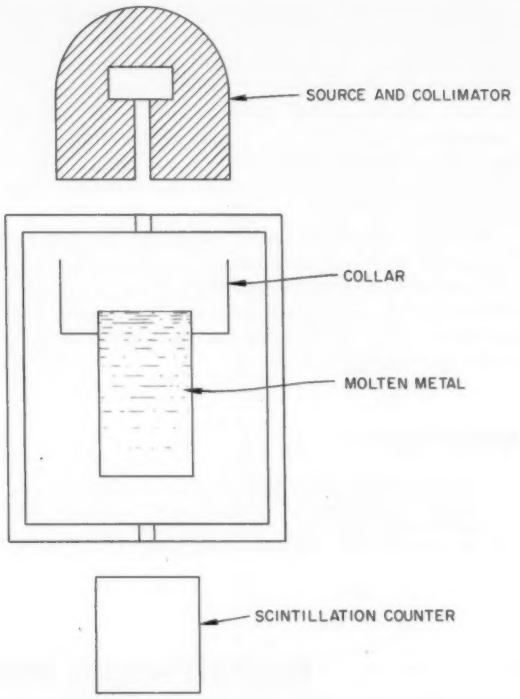

Fig. 2 Equipment for determining temperature of a molten metal by measurement of the transmitted gamma-radiation intensity.

With good equipment, continuous and high-precision recording of gamma radiation is possible. In the tests on the method, the gamma beam was shaped by a system of adjusted collimators. After it passed through the metal, it was counted by a scintillation detector [NaI(Tl) crystal and photomultiplier]. In the electronics circuit the electric pulses were amplified, adjusted, and integrated. The precision of the equipment for recording radiation intensity was 0.5%. Two to five temperature readings can be made with a 100°C change in the molten-metal temperature in the range between the melting and boiling points.

Table 1 OPTIMUM THICKNESSES OF MOLTEN METAL FOR MEASURING TEMPERATURE BY TRANSMISSION OF GAMMA RADIATION FROM ^{60}CO

Metal	*d*, cm	Metal	*d*, cm
Li	78	Ag	4
Na	37	Cd	5
Mg	20	Sn	6
Al	14	Au	2
K	41	Pb	3
Zn	5	Bi	4

(Martha Gerrard)

RADIOMETRIC DETERMINATION OF MELTING POINT

H. Kobayshi* has described a radiometric technique that may be useful for determining melting points. It consists in placing crystals of the solid whose melting point is to be determined on an alpha source connected to a thermocouple and determining the temperature at which the ionization current induced by the source decreases abruptly. Kobayshi was working with a Ra D-E-F source and observed that the current produced by the alpha particles in a thin, differential ionization chamber decreased abruptly when some ice crystals resting on the source melted. This was due to the liquid spreading out over the source so that a larger area was covered than when the crystals were present,

and thus more of the alpha radiation was absorbed by the material. He then determined the temperatures of abrupt current change for two other substances — benzene and *p*-xylene — and found them to be +5.5 and +13°C, respectively, i.e., the melting points of these two substances. (MG)

*A New Method of Determining the Melting Point of Powdered Materials by Alpha-Ray Absorption, *Scientific Papers of the Institute of Physical and Chemical Research (Tokyo)*, 51(1): 1-4 (1965).

Tracerlab Radioisotope Facilities*

Abstract: The Tracerlab Western Division radiochemical facilities and program are described.

*Based on Tracerlab literature and reviewed by W. J. Schwarz of Tracerlab's Western Division before publication.

Tracerlab's major radiochemical facilities are located in Richmond, Calif., with Eastern Division facilities, in Waltham, Mass. The California facilities consist of several laboratories, and for two decades a broad radioisotope program has been carried out there. The Western facility is shown in Fig. 1.

Fig. 1 Tracerlab Western facility.

Laboratories

Tracerlab radioisotope work is carried out in four sections of the Western facilities. The level of radioactivity handled is a direct function of the sample characteristics, including physical configuration, specific activity, and toxicity. In general, the levels vary from millicurie to microcurie. For special projects, samples with activities up to 10 curies are handled and stored. The Radiochemical Analysis Laboratory is made up of five modules, each 384 sq ft in area, and a common work area. It is equipped with all the usual laboratory facilities, including chromatographic ion-exchange equipment. The Low Level Laboratory is designed for handling samples with picocurie levels of activity and is isolated from the rest of the building to prevent cross-contamination. The Radiation Wing, in another part of the building, is designed for handling curie levels of activity and is kept under a slight negative pressure to ensure that no radioactive material leaks to the remainder of the plant. The Ultramicroanalytical Facility contains equipment developed for work on both optical size and submicron-size radioactive particles.

All needed radiation measurement facilities are available—counting rooms with argon and methane flow proportional end-window counters, 2π and 4π internal flow counters, end-window low-background Geiger flow counters, a refrigerated automatic liquid scintillation counter, gross gamma NaI(Tl) crystal assemblies with and without wells, NaI(Tl) crystal spectrometer assemblies, including a low-background unit and a thin crystal for low-background X-ray counting, and Frisch grid- and surface-barrier silicon semiconductor detectors for low-level alpha spectroscopy. Associated data-handling equipment includes punched tape from multichannel analyzers and a tape-to-IBM-card converter.

Program

Tracerlab currently has the capability of determining 71 elements and a total of 161 radionuclides (Table 1). The half-lives of the radionuclides which have been or are being determined are shown in Table 2. Sequential separation schemes for a large number of different combinations of elements have been devised to obtain the maximum number of analytical results from a single sample. In some programs, analyses for 21 elements, comprising 44 isotopes with half-lives as short as 0.5 day, have been made routinely. Carriers or radioactive tracers are used in most procedures to ensure accurate and precise results. Alpha, gamma, and X-ray spectrometry and various beta counting techniques are used for resolving many different isotopic mixtures. Many of the counting data are recorded on punched tape for direct input to an IBM-1130 computer.

Table 1 RADIONUCLIDES DETERMINED BY TRACERLAB

^{3}H	^{7}Be	^{13}N	^{14}C	^{18}F	^{22}Na	^{24}Na	^{28}Mg	^{32}P
^{33}P	^{35}S	^{36}Cl	^{40}K	^{41}Ar	^{45}Ca	^{47}Ca	^{44m}Sc	^{46}Sc
^{47}Sc	^{48}Sc	^{51}Cr	^{52}Mn	^{54}Mn	^{56}Mn	^{55}Fe	^{59}Fe	^{58}Co
^{56}Co	^{57}Co	^{58}Co	^{60}Co	^{57}Ni	^{59}Ni	^{63}Ni	^{66}Ni	^{64}Cu
^{67}Cu	^{65}Zn	^{72}Ga	^{71}Ge	^{77}Ge	^{76}As	^{75}Se	^{86}Rb	^{85}Sr
^{89}Sr	^{90}Sr	^{91}Sr	^{88}Y	^{90}Y	^{91}Y	^{89}Zr	^{95}Zr	^{97}Zr
^{92}Nb	^{95}Nb	^{99}Mo	^{103}Ru	^{106}Ru	^{102}Rh	^{110m}Ag	^{111}Ag	^{112}Ag
^{109}Cd	^{113m}Cd	^{115}Cd	^{115m}Cd	^{114}In	^{113}Sn	^{125}Sn	^{124}Sb	^{125}Sb
^{129}Te	^{131}Te	^{132}Te	^{125}I	^{131}I	^{133}I	^{134}I	^{135}I	^{134}Cs
^{136}Cs	^{137}Cs	^{138}Cs	^{139}Cs	^{133}Ba	^{140}Ba	^{140}La	^{139}Ce	^{141}Ce
^{143}Ce	^{144}Ce	^{143}Pr	^{147}Nd	$^{143,4}Pm$	^{147}Pm	^{153}Sm	^{156}Eu	^{159}Gd
^{160}Tb	^{161}Tb	^{166}Ho	^{170}Tm	^{169}Yb	^{175}Yb	^{177}Lu	^{175}Hf	^{181}Hf
^{182}Ta	^{181}W	^{185}W	^{187}W	^{188}W	^{186}Re	^{188}Re	^{192}Ir	^{199}Pt
^{195}Au	^{196}Au	^{198}Au	^{199}Au	^{203}Hg	^{200}Tl	^{201}Tl	^{202}Tl	^{204}Tl
^{203}Pb	^{210}Pb	^{210}Bi	^{210}Po	^{222}Em	^{226}Ra	^{227}Th	^{228}Th	^{230}Th
^{231}Th	^{232}Th	^{234}Th	^{231}Pa	^{233}Pa	^{232}U	^{233}U	^{234}U	^{235}U
^{236}U	^{237}U	^{238}U	^{240}U	^{237}Np	^{238}Np	^{239}Np	^{236}Pu	^{238}Pu
^{239}Pu	^{240}Pu	^{241}Pu	^{241}Am	^{243}Am	^{242}Cm	^{244}Cm	^{252}Cf	

Table 2 HALF-LIFE DETERMINATIONS BY TRACERLAB

^{109}Cd	^{147}Nd	^{55}Fe
^{203}Pb	^{187}W	^{239}Np
^{231}Th	^{54}Mn	^{59}Fe
^{7}Be	^{90}Y	^{236}Pu
^{196}Au	^{199}Au	^{64}Cu
^{237}U	^{131}I	^{141}Ce
^{204}Tl		

Samples are analyzed for fission products, neutron-induced or other activation products, the actinide elements, and naturally radioactive elements. Data are obtained from nuclear test debris, from nuclear rocket test samples, and from samples collected for studies of radioactivity in the biosphere, such as milk, bone, vegetation, and water.

Tracerlab is using a great variety of accelerators and reactors. Among these are: High Power Water Cooled Test Reactor, General Electric Company—Vallecitos Nuclear Center, Pleasanton, Calif.; TRIGA, Aerojet–General Nucleonics Corporation, San Ramon, Calif.; and the 86-in. Cyclotron at Oak Ridge National Laboratory. An example of activation analysis work is an analysis that was made of dust deposited in a residential area to determine whether it came from a nearby industrial plant. Activation analysis of dust samples collected downwind from the plant after plant process streams had been labeled with nonradioactive rare earths showed conclusively that particulate material from the plant contributed less than 6% to the local dust fall. In an investigation of the feasibility of using simulator elements as tracers to determine the potential hazard involved in atmospheric reentry of SNAP devices, Tracerlab analyzed blanks and collection mediums. Programs for determination of trace impurities in high-purity crystals and semiconductors have been performed.

Trace elements have been determined by neutron activation analysis in terphenyl used as a reactor coolant and in packaging material for the food and drug industry. The composition of isolated stainless-steel microspheres weighing 10^{-9} g each was determined in another program. (Martha Gerrard)

PORTABLE ^{192}Ir RADIOGRAPHIC SOURCE

A portable (51 lb) gamma irradiator containing up to 100 curies of ^{192}Ir is manufactured by Picker X-Ray Corporation (White Plains, N. Y.). Rugged in construction and with a directional beam, it can make radiographic inspection of pipes in the field as well as in the laboratory. Its fail-safe control system and depleted uranium shield offer maximum protection to the operator. With a 20-curie loading, it can radiograph an 8-in.-OD, $^3/_8$-in.-wall, steel pipe in 15 sec. A mounting stand, slide-rule exposure calculator, and radiation badges and dosimeters are available as accessory equipment.

(Martha Gerrard)

RESTORATION OF PHOTOGRAPHS BY NEUTRON ACTIVATION

Neutron irradiation of badly faded and stained photographs, followed by autoradiography, restored the image of both negative and positive prints. A reactor flux of 10^9 n/(cm^2)(sec) was used to activate the image silver to ^{108}Ag (2.3-min half-life), whose 1.57-Mev beta radiation produced an intensified image on a fresh radiation-sensitive surface. The degree of intensification was controlled by balancing the initial level of activation and the duration of the autoradiographic contact. The method was successful if even traces of image silver remained, provided that nonimage silver and halides were absent. [Eugene Ostroff, *Science*,154: 119–123 (1966)]. (MG)

RADIOISOTOPE THICKNESS GAGE FOR HOT-ROLLED METAL (E. GERMANY)

Radioisotope gages, which make no contact with material being measured, should determine the thickness of hot-rolled metal more accurately and with fewer handling problems than ordinary gages. In East Germany a thickness gage based on the attenuation of the bremsstrahlung from a 2-curie ^{85}Kr/Au source has been developed[1] for use with hot sheet metal from 1 to 10 mm thick. The precision of the measurement is ±1.0% for 6-mm-thick material. A heat shield is placed between the scintillation crystal in the detector and the hot metal. A similar hot-rolled-metal thickness gage containing ^{137}Cs is manufactured by the Hitachi Company in Japan.[2] (MG)

1. J. Holzhey, E. Oertel, F.-W. Wagner, Radiometric Thickness Gage for Hot-Rolled Material Between 1 and 10 mm (in German), *Isotopenpraxis*, 3: 33–34 (1967).
2. *Isotopes and Radiation Technology*, 5(1): 24 (1967).

Section

III

Isotopes and Radiation Technology

Food Irradiation

Potential Role of Radiation in Alleviating Some World Food Problems

By K. F. MacQueen*

Abstract: Irradiation, the first revolutionary technique for food preservation in over 150 years, produces many useful effects, e.g., inhibition of sprouting in vegetables, delay of ripening in fruits, control of insect infestations in cereals and dried foods, and destruction of microorganisms in fish, meats, and other foods. How these useful effects would improve the storage and distribution of various food products that may be largely wasted but are vitally needed by those suffering from hunger and malnutrition is illustrated here. With increased support for research and training, the new technology of food irradiation is expected to contribute to alleviating the food deficiency that affects over half the world's population.

As we in Canada celebrate our Centennial Year, it is an opportune time to reflect not only on our progress and problems but also on those of the world at large. The revolution in communications and transportation we have experienced in the last 50 years has made us more aware of the problems of the global community. We are becoming increasingly involved in the world's affairs. The most important problem that we and other nations of this planet must attempt to solve in the remaining decades of this century is that of increasing world food supplies to meet the challenge of a rapidly growing population, which will double by 2000 A.D. The solution to this problem is vital to the future stability of the world.

The use of radiation is the first revolutionary technique for food preservation since Appert discovered thermal canning more than 150 years ago. Other well-known preservation processes—drying, salting, fermentation, freezing, and smoking—are centuries old. Irradiation is not intended to replace existing preservation processes but may be used in conjunction with methods in current use, such as refrigeration and drying. Irradiation should be combined with proper storage and packaging techniques to ensure that maximum benefits are obtained.

World Food Problem

Let us consider the magnitude of the world food problem.[1-7] The startling fact is that over 50% of the world's population suffers from hunger, malnutrition, or both. Hunger may be defined as "undernutrition in which there is an inadequate supply of food available to the individual." Estimates indicate that up to 500 million people of the 3400 million in the world are underfed. Malnutrition, on the other hand, implies that the diet is lacking in quality or is unbalanced because it includes too many starchy foods and too few of the nourishing foods like meats, milk, fruits, and vegetables. These two problems often occur together.

Hunger and malnutrition have both social and economic implications. A hungry, undernourished individual is a liability to society. He is very susceptible to disease, which compounds his problems, and his ability to work and study is quite restricted. Since he represents so many millions whose initiative and spirits are dulled by their deprivation, he hinders rather than helps economic and social progress in his part of the world. In a broader political sense, a stable world is difficult to envisage until this immense human suffering can be alleviated. In fact, the ideal of individual freedom may be very empty for those who have insufficient food for themselves and their children.

The Food and Agriculture Organization (FAO) of the United Nations finds it convenient to divide the world into two groups when considering the contrast between qualities of diet existing in different parts of the world:

*Atomic Energy of Canada Ltd., Commercial Products, Ottawa; paper reprinted, with minor editorial changes and by permission, from Canadian Report AECL-2873, prepared for Canadian Nuclear Association Conference, Montreal, May 28–31, 1967.

Group I: the low-calorie areas, averaging 2150 calories per day per person, which include the Far East, the Near East, Africa, and Latin America except the River Plate countries (Argentina, Uruguay, and Paraguay)

Group II: the adequate-calorie areas, averaging 3060 calories per day per person, which include Europe, North America, the River Plate countries, and Oceania

Although the contrast in total calories per person per day is striking — 2150 vs. 3060 — the contrast between consumption of animal proteins is even greater, with Group I showing only 9 g daily per person compared to 44 g daily for each person in Group II (Table 1). The Group I countries consume chiefly cereals and starchy roots, whereas the Group II countries consume about the same amount of cereals and starchy foods but 6 times as large a quantity of animal products (meat, milk, eggs, and fish).

Table 1 AVERAGE FOOD CONSUMPTION OF THE TWO GROUPS OF THE WORLD POPULATION

Food	Daily amount, g, per person at retail level	
	Group I	Group II
Total proteins	58	90
Animal proteins	9	44
Total fats	34	106
Cereals	389	328
Starchy roots	189	316
Vegetables and fruits	169	362
Milk	79	573
Meat	30	152
Fish	24	34
Eggs	4	30
Legumes and nuts	53	16
Sugar	29	88
Fats and oils	12	47

The low level of protein in the diets of the developing countries contributes to an incidence of deficiency diseases, which are rare in the developed countries. The most common deficiency disease is kwashiorkor in young children when they are transferred from their mother's milk to a diet of starchy foods such as yams, sweet potatoes, or maize flour. In Brazil, for example, the FAO reports that about 300 thousand children below the age of two die annually of malnutrition.

Malnutrition and hunger also contribute to an increased susceptibility to other diseases and to a shorter span of life. The expected life span in India is only 38 years, compared to 70 years in the United Kingdom. The infant mortality rate in India is 100 per 1000 — more than 4 times that in England and Wales. The view of the medical profession is that better food is the only cure for deficiency diseases.

Adding to the present problem of food deficiency, which affects over half the world, is the rapid rate of population growth (Fig. 1). Let us look at the pattern of growth from the first century A.D. At the time of the birth of Christ, the world's population was estimated at 200 to 300 million. This population doubled to 500 million in 16 centuries, 2 centuries later doubled again, to 1 billion, and in the next hundred years to 2 billion. With the present world population at 3.4 billion and the rate of growth at over 1 million per week, United Nations experts estimate that the world population will be 6 to 7 billion by the year 2000 A.D. (Table 2). About four-fifths of this projected increase will occur in the less developed countries, where food shortages already exist. On the other hand, the percentage of the world population in the developed nations, including North America and Europe, will decline. The population of Latin America will be almost double that of North

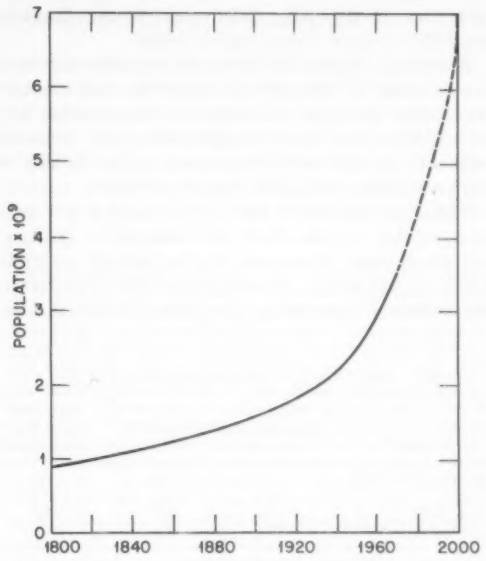

Fig. 1 World population, 1800 to 2000 A.D.

Table 2 UNITED NATIONS "HIGH" POPULATION PROJECTIONS TO THE YEAR 2000 A.D.

Area	1970		2000	
	Number × 10^6	Percent of world total	Number × 10^6	Percent of world total
Asia (excluding Soviet Union and Japan)	1870	53.4	3717	59.2
Latin America	265	7.6	592	9.4
Africa	294	8.4	517	8.2
Europe (excluding Soviet Union)	457	13.3	568	9.1
North America	225	6.4	312	5.0
Soviet Union (Asia and Europe)	254	7.3	379	6.1
Japan	110	3.1	153	2.5
Oceania	19.4	0.5	29.3	0.5
World total	3500	100	6280	100

America by the year 2000 even though these two populations were about equal in 1960.

A further aspect of the problem is the unbalanced distribution of agricultural production and income in the world. While the less developed areas of the world have 70% of the world's population, they contribute only 40% of the world's agricultural production and earn a meager 20% of the world's income.

The FAO estimates that an increase in per capita consumption of one-third is required to achieve a minimum level of adequate diet for the undernourished areas of the world. The estimated food requirements for undernourished areas are given in Table 3, taking

Table 3 ESTIMATED FOOD REQUIREMENTS IN 2000 A.D.

Area	Index* of consumption per person	Population Index*	Index* of total food requirements
Asia and Far East	167	243	406
Africa	128	202	259
Near East	117	262	307
Latin America†	105	322	338

*Indexes based on 100 for about 1958.
†Excluding River Plate countries.

into account future population growth and an objective of providing in the year 2000 a minimal diet of 2400 calories per person per day with 20 g of animal protein. To achieve this objective, the supply of food must be increased four times in Asia and the Far East, between three and four times in Latin America, three times in the Near East, and between two and three times in Africa. For the world as a whole, food supplies would have to triple by the turn of the century. For each additional 100 million mouths in the Far East, 16 million tons of cereals, 3 million tons of legume products, 7 million tons of fruits and vegetables, 3 million tons of meat, eggs, and fish, and 3 million tons of milk annually will be required.

Possible Solutions

How can the wealthy nations assist their less fortunate neighbors in solving their food problems? It is generally agreed that a policy of supplying a large amount of food aid cannot solve the world food problem on a long-term basis. The best approach is to help these less developed countries help themselves. They must be encouraged and helped to control their population growth and to apply modern agricultural technology to improve the production, storage, and distribution of food supplies.

Possible methods of increasing food supplies include:

1. *Extending areas under cultivation.* Prospects for this are very limited since most of the arable land is already in use, particularly in Asia. In the long term — after the year 2000 — the availability of low-cost nuclear power offers the possibility of irrigating arid lands.[8]

2. *Increasing crop yields.* Prospects are much brighter for increasing food supplies by applying modern agricultural technology. Experience in Mexico, for example, has shown that wheat yields can be doubled by use of chemical fertilizers and pest controls, improved varieties of seed, and better management.[9] Mexico now produces sufficient wheat for her needs. Similarly, the yield of rice per acre in Japan is about triple that of India, largely as a result of using fertilizers.

3. *Increasing protein production.* Fish now contribute about 10% of man's total intake of animal protein. Since three-quarters of the earth's surface is covered with water, the potential of fish as a food source in providing relief for protein-short regions may be substantial, particularly since it would not depend on limited land-based resources. The successful development of a fish-protein concentrate for human consumption makes possible a wider distribution of this important source of protein.

Animals tend to be inefficient in converting feed to food. For example, in North America most of the plant material is fed to livestock to provide a diet in which one-third of the calories is composed of meat, milk, or eggs. This represents a consumption of 11,000 primary calories to achieve an average diet level of 3150 calories. One encouraging factor is that animals such as cows and sheep can convert food material not suitable for use by man.

More exotic processes include the production of protein from the action of microorganisms on petroleum fractions and from algae farming. These processes have very-long-term potential only.

4. *Improved preservation, storage, and distribution of food actually produced.* This area merits more attention than it has received, i.e., insurance that the food produced in a given country or area is adequately preserved, thereby reducing spoilage to a minimum and permitting a wider distribution within the food-deficient area. This is a particularly attractive method since it makes possible more efficient use of the food already produced locally and of additional food that will result from application of the first three methods.

Radiation treatment may play a useful role in this area of preserving fruits, vegetables, meats, and fish, the vitally needed nutritious foods. The majority of new food supplies must be generated within the food-deficient areas since the quantity of food required to feed the additional population of the undernourished world by 1980 is about equal to the present production of North America and Western Europe combined. Conservation of the tremendous quantities of locally produced food that would go to waste otherwise will be more economical than the shipment

of surplus food over long distances from the developed countries. Further, the tonnages required could not be handled by present shipping and marketing facilities.

Food Spoilage

Let us consider the magnitude of the food-spoilage problem in order to realize the merits of improved preservation, storage, and distribution. The FAO estimates that one-fifth of the world food crop planted by mankind is destroyed by insects, microorganisms, and other pests. The losses in specific areas may be higher—up to 50%—and are greatest in those parts of the world where the population is already undernourished and can ill afford to lose any part of the food supply. In tropical areas the products rich in vitally needed animal protein—meat, milk, eggs, and fish—decompose in a matter of hours at high temperatures.

The Chairman of India's Council for Scientific and Industrial Research has indicated that more than 50% of the food in India is lost from all causes and that the value of these losses is almost twice the national budget.[10] The Central Food Technology Research Institute at Mysore reports that 30% or more of India's annual crop of 15 million tons of fruits and vegetables is lost through improper storage and transportation facilities.[11] Losses of rice in India have been estimated as approaching 3 million tons annually.

In Africa, losses of dried fish resulting from insect infestation are estimated to be as high as 50% of the weight of the finished product.[12] In the Congo a scientifically controlled test showed that 50% of the sorghum (a staple part of the Central African's diet) was destroyed by insects during 12 months of storage.[10] Postharvest losses in Africa were estimated at about 30%.

In Argentina, nearly a third of the food harvested spoils before reaching the consumer.[10] Argentina estimates her wheat losses in storage to be equivalent to 880 million lb of bread and her overall annual losses at $350 million. In Chile, postharvest losses of vegetables are 50% and of fruits, 40%.

If this great spoilage of food could be reduced significantly—say by one-half—then millions of the hungry or malnourished could be fed. For example, 55 million Africans could be fed each year from the grain destroyed there by pests or microorganisms. In terms of world production of cereal grain, a 50% decrease in losses would result in protein savings of 9 million tons—enough to feed nearly 300 million people. Further,[7] if a third of the food losses in tropical areas could be eliminated, many countries would have enough to meet their additional food requirements for at least a decade.

Preservation Effects of Radiation

Let us consider the potential role of irradiation in the application of modern technology of foods.

In India a research program has been initiated, at Trombay, on the application of ionizing radiation for the preservation of perishable foods and the disinfestation of stored grain. This program is receiving top priority because, as stated[13] in an Indian publication,

> The potentialities for radiation processing of foods with ^{60}Co gammas are immense: They are being increasingly recognized and extensively studied the world over. This is because ionizing radiation is lethal to microorganisms, parasites and insect pests and can, like refrigeration and freezing, be used for preservation of food in the uncooked state. The need for study and application of radiation processing is all the greater in tropical regions like India where problems of grain infestation, damage to perishable foods and incidence of food-borne pathogens are often severe and where handling, packaging, transportation and storage facilities are frequently inadequate. Any effort, therefore, aimed at minimizing such damage is bound to help the country to alleviate its food problem.

Irradiation, a revolutionary technique for food preservation, can achieve a number of useful effects:

Inhibition of sprouting or growth of root crops, e.g., of potatoes, onions, carrots, garlic, sugar beets

Delay of ripening, e.g., of mushrooms, bananas, papayas, mangoes

Killing of parasites, e.g., *Trichinella* in pork, tapeworm in beef

Destruction of insects, e.g., in grain and grain products, fruits, and dried foods, proper packaging being necessary to prevent reinfestation

Destruction of microorganisms: (1) spoilage bacteria, fungi, or molds in strawberries, fish products, fresh poultry, meats (pasteurization, i.e., destruction of 99% or more of the organisms extends shelf life, best results being obtained with refrigeration); (2) food-borne pathogens, e.g., *Salmonella* in egg products, poultry, meats; and (3) all organisms, or sterilization, by high doses

Modification of physical properties, e.g., to decrease cooking time of dehydrated vegetables[14]

Other unique advantages of radiation processing of food are:

1. Radiation is the only method that can be applied to foods through any type of packaging materials, including paper, plastic, wood, and metal cans. Some of these materials could not withstand any heat processing. The fact that radiation can be applied after packaging is a great advantage since recontamination or reinfestation of the product is avoided.

2. Foods can be treated without cooking the product. The temperature rise is only a few degrees even at high-dose sterilization. This ability to treat food products in their natural state is particularly beneficial since experience has shown that consumers in

developing countries will most readily accept foods which remain essentially unchanged.

To achieve the optimum benefit of irradiation as a preserving technique, proper packaging and storage are essential, particularly where the product is vulnerable to insect infestation or spoilage by microorganisms. Other well-established techniques may be combined with irradiation to enhance food preservation.

Potential International Applications

Let us now consider some examples of how irradiation might be applied to help alleviate world food problems. Some of the projects mentioned below were initiated specifically with the world food problem in mind, while others were undertaken from the commercial viewpoint. Regardless of the objective, the results illustrate how irradiation will improve the preservation and distribution of food products.

1. *Control of insect infestation in dried fish and grain.* Reports from surveys made in Mali,[12] Nigeria,[15] and northern Rhodesia[16] indicate tremendous losses (up to 50%) from insect infestation of dried fish. The total annual losses incurred through insect spoilage of dried fish are estimated at more than 10 thousand tons ($3 to $4 million) in Mali and the same in Nigeria. These losses would supply the protein needs (FAO target of 20 g per person per day) of several million Africans each year.

Aref,[12] on assignment for FAO in the Republic of Mali, obtained results in preliminary experiments which indicate a good potential for preserving this product with irradiation and proper packaging to prevent reinfestation. Three lots of severely infested dried fish purchased in the Mopti dried-fish market were packaged in polyethylene and then irradiated at doses of 23, 105, and 530 krads. Little or no flavor change was observed by a panel composed of local tasters. Immediately after the irradiation the insects in the samples exposed to 105 and 530 krads appeared to be dead, and 15 days later no live insects were found. In the samples exposed to 23 krads, only several adults and larvae were found after 15 days.

Studies made in Canada on the effect of radiation on insects[17] found in stored products and on the effect of insect-control doses on the quality of wheat and rice[18,19] have given favorable results. A petition for the clearance of wheat and wheat products is being prepared.

2. *Control of spoilage in fruits and vegetables.* Encouraging results have been obtained with the irradiation of selected fruits and vegetables grown in tropical regions. The College of Tropical Agriculture at the University of Hawaii[20] has reported excellent results with radiation treatment of papayas. A dose of 75 krads combined with hot-water treatment appears to delay ripening and inhibit fungal spoilage sufficiently to double the shelf life at room temperature, i.e., from 3 to 6 days. At the same time, this dose is more than three times the 21 krads found adequate for disinfestation to satisfy requirements for entry of fruits and vegetables from Hawaii into the continental United States.

This process appears to have excellent commercial possibilities in that the 75 krads plus hot-water treatment could replace the fumigation plus hot-water treatment now used for papayas air-shipped at room temperature. An even greater extension of shelf life may be realized when papayas are shipped at refrigeration temperatures. As a result of the extended shelf life and the improved quality from irradiation, which will make possible the shipment of the product to new markets, the exports of papayas from Hawaii may, by 1970, reach 20 million lb annually ($5 million value), representing an increase of 400% over 1965 exports. This is an excellent example of the great potential benefits to be realized when a product, normally consumed locally, can be made available to the export trade after radiation treatment.

Maxie,[21] in his extensive studies on fruit irradiation at the University of California, has reported favorable results with bananas. When Gros Michel, the important commercial variety grown in Central America, was irradiated to low doses prior to initiation of the ripening process, ripening was delayed significantly, e.g., 16 to 20 days by 20 krads. When the fruit did ripen, it remained edible 2 to 3 days longer than normal. The ripening process can be initiated in the irradiated fruit, when desired, by exposing it to ethylene gas, as in normal commercial practice. Since bananas that ripen during shipment are very susceptible to impact or vibration injury, the use of radiation makes it possible to delay the ripening process until after shipments are completed.

Irradiation of fruits and vegetables grown in India has been studied by Dharkar and Sreenivasan[22] of the Atomic Energy Establishment, Trombay. Ripening of mangoes stored at ambient temperature was delayed 6 days by a dose of 25 krads. An additional 6 days' delay in ripening, i.e., a total of 12 days, was achieved by a combination of skin-coating (emulsion made of an acetylated monoglyceride preparation) and irradiation. A dose of 20 to 25 krads achieved a 5-day delay in ripening of tomatoes, guavas, and sapotas (sapodillas). Semidried bananas (40% moisture) packaged in polyethylene and irradiated at 500 krads kept well for at least 3 months, and the product was superior to dehydrated fruit (10% moisture) with regard to susceptibility to mold infection, color, flavor, retention of nutrients, and reconstitutability. Sprouting was inhibited in potatoes by a 10-krad dose and in onions by 6 krads, resulting in an extension of shelf life to 32 and 24 weeks, respectively, from the 8 weeks for unirradiated controls. Combinations of heat and radia-

tion were used successfully for sterilization of mangoes, guavas, sapotas, apples, and orange juice.

Irradiation of citrus fruits appears to hold some promise for reducing spoilage losses from harvest to consumer based on experiments being conducted in the United States[23] and Israel.[24] Spoilage losses in the annual fresh-fruit market in the United States for the years 1959–1963 were estimated to be more than $8 million for oranges and over $5 million for grapefruit.

In Canada we have had promising results with the irradiation of potatoes, onions, mushrooms, strawberries, apricots, peaches, pears, and plums.[25] We have already obtained clearance for potatoes (1960) and onions (1965), are preparing a petition for clearance of strawberries, and expect to submit a petition on mushrooms early in 1968.

3. *Quarantine control of viruses in carcasses of infected animals.* The FAO[26] stated in 1962 that, if the animal diseases which plague a vast majority of the world's livestock could be brought under control, there would be no difficulty in achieving future animal-protein requirements, at least to 1975. Total losses in areas with no animal health programs appear to exceed 40%.

Foot-and-mouth disease is a malady of great economic significance which affects cattle, sheep, goats, and pigs. For example, the Health of Animals Branch, Federal Department of Agriculture, estimates a $900 million loss to the country resulting from the outbreak that occurred in Canada in 1952. Most of this loss was attributed to the loss of markets for agricultural products resulting from the quarantine imposed following this outbreak. The actual cost of eradication, involving the slaughter of a few thousand animals, was relatively small—about $1 million. In Europe, during the 1951–1952 wave, this disease caused about $6 million damage. Foot-and-mouth disease is almost constantly present in the continent of Europe and in countries of South America and is indigenous in many parts of Africa and Asia. Since humans, under certain conditions, are susceptible to this disease, consumption of meat from infected animals could present a health hazard.

Other virus diseases that pose a threat to world food supplies include rinderpest, which is deadly to cattle, and African swine fever. These viruses have been spread in frozen animal products.

In the study undertaken by Massa[27] in Italy, the objective was not eradication, which is almost impossible to achieve in some parts of the world because of wild life and the widespread nature of the problem, but radiation treatment of products from infected animals such as meat, bones, glands, hair, and hides in order to inactivate the foot-and-mouth disease virus. Massa's results were encouraging: He found that a sterilizing dose of radiation would successfully inactivate the foot-and-mouth virus in the tissues of experimentally infected animals.

The implications of this finding are important for developing countries. For example, large regions in Africa could supply large quantities of meat for export to other countries, but importation of their products is restricted because of the health situation of their animals. Irradiation appears to be the only technique available at present which is capable of eliminating viral agents from the animal products and yet maintain them in the original raw state.

Radiation has already been used successfully in Australia to treat baled goat's hair to eliminate the anthrax organism, *Bacillus anthracis*.

In Canada the Virus Laboratory, Department of National Health and Welfare, has extensively studied the use of gamma radiation for the preparation of virus vaccines.[28] Results have been favorable, and the process has been patented.

4. *Control of* Salmonella *in foods and animal feeds.* The communicable disease salmonellosis is a major public health problem in both the developed and developing parts of the world.[29] It has received much attention in the more advanced countries; in the developing countries it is probably overshadowed by illness associated with malnutrition. The term "salmonellosis" normally refers to an outbreak of food poisoning in the human, caused by some species of *Salmonella* and resulting in gastrointestinal disorders of varying degrees of severity. The disease is readily transmissible from animal to man. Healthy adults may suffer no symptoms but may be carriers of the disease.

Bowmer[30] of Vancouver, B. C., in an extensive review of the problem, illustrated the cycle of *Salmonella* infection (Fig. 2) from animal feed, to animals and poultry, and thence to foods consumed by man. Conversely, man may transmit the disease to livestock. Control of the disease requires breaking the cycle at several points. Improved sanitation, milk pasteurization, and chlorination of water[31,32] have resulted in a steady decline in the number of cases of typhoid fever (caused by *Salmonella typhosa*) in the United States during the past quarter century. However, during the same period, human salmonellosis other than typhoid has increased rapidly (Fig. 3), partly because microbiological control measures have not kept pace with the great technological progress achieved in the preparation and distribution of feeds and foods that act as vehicles to disseminate the disease. In 1965 the sources of nonhuman *Salmonella* isolations in the United States included turkeys, chickens, other fowl, cattle, swine, other animals, eggs and egg products, other foods, animals, animal feeds, and water (Fig. 4). It is significant that over 50% of the isolations were found in poultry. In Canada the Food and Drug Directorate has legislated against the sale of egg products and foods containing egg products contaminated with *Salmonella*.

Irradiation was discussed in a panel sponsored by IAEA to report on the radiation control of harmful organisms transmitted by food and feed products with particular reference to *Salmonella*.[33]

In extensive studies[33–37] on irradiation as a method of controlling *Salmonella* in food and animal feeds in Canada, the United States, United Kingdom, the Netherlands, and Denmark, results have been most encouraging. In general, doses of about 500 krads applied to frozen or fresh foods and a dose of 800 krads applied to dried feeds or foods will decrease the *Salmonella* population by a factor of about 10^3. Further, the organoleptic acceptability and the wholesomeness of the products appear satisfactory. When fresh poultry meat is treated with a dose of 500 krads to control *Salmonella*, for example, there is the added advantage that the shelf life of the iced product is extended from the normal 6 to 8 days to 18 to 20 days.

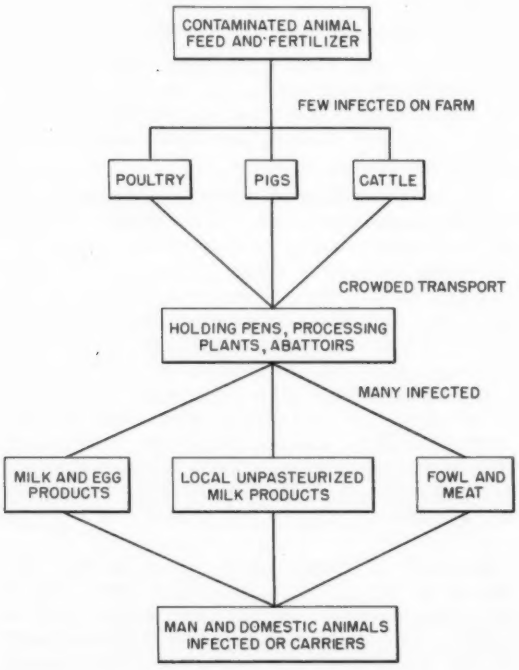

Fig. 2 Transmission of salmonellosis.

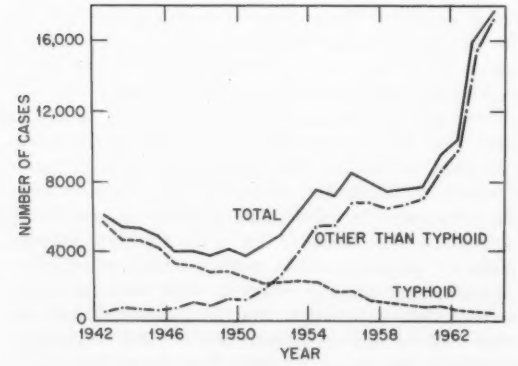

Fig. 3 Reported incidence of human salmonellosis in the United States, 1942–1964.

In Canada, AECL is supporting studies on the use of radiation to control *Salmonella* in iced fresh chicken (a joint Canadian–U. S. venture) and in animal feeds containing protein supplements such as meat meal and/or fish meal. We plan to support a further study on irradiation of egg products.

Fish meal is of special interest because it is becoming a very large item in international trade. Peru,[38] for example, has increased her exports of this product from 28 thousand metric tons in 1956 to over 700 thousand metric tons in 1961. This meal is distributed to at least 15 countries in North America, South America, and Europe and is incorporated into animal feeds. In 1961 the total world production of fish meal was approaching 2 million metric tons.

5. *Preservation of fresh fish and marine products.* The growth in the world catch of fish and in the international trade of fish and fishery products in the postwar period has exceeded world population growth. The world's catch was estimated[39] at more than 100,000 million pounds in 1964. However, distribution of fresh fish is severely restricted by the rapid rate of spoilage even at refrigerator temperatures. Better methods of preservation are vital to improve the distribution of this high-protein food, particularly to those populations not living close to fishing grounds and who may suffer from protein malnutrition.

Studies conducted at the Fisheries Research Board, Halifax, N. S., showed that the shelf life of iced scallops, haddock, and lobster may be doubled by a dose of 75 krads.[39–42] Favorable results were also obtained in the irradiation of freshwater fish (whitefish) by the Federal Department of Fisheries, Winnipeg,[43] the iced shelf life of this fish being extended 1 to 2 weeks by doses from 75 to 150 krads (Table 4).

The U. S. Atomic Energy Commission is conducting an extensive program on fish irradiation[44] and has reported promising results on a wide spectrum of marine products including shrimp, crab, haddock, and clams (Table 4).

Work in India[45] has also shown encouraging results on local fishery products. Bombay duck (a fish of commercial importance) keeps only a few hours at ambient temperatures and 2 to 3 days when packed in ice. When it is irradiated to a pasteurizing dose of 400 krads, its shelf life is extended to 3 weeks at 10 to 12°C and to 6 weeks at 0 to 4°C. Semidrying to 40% moisture plus irradiation extends the shelf

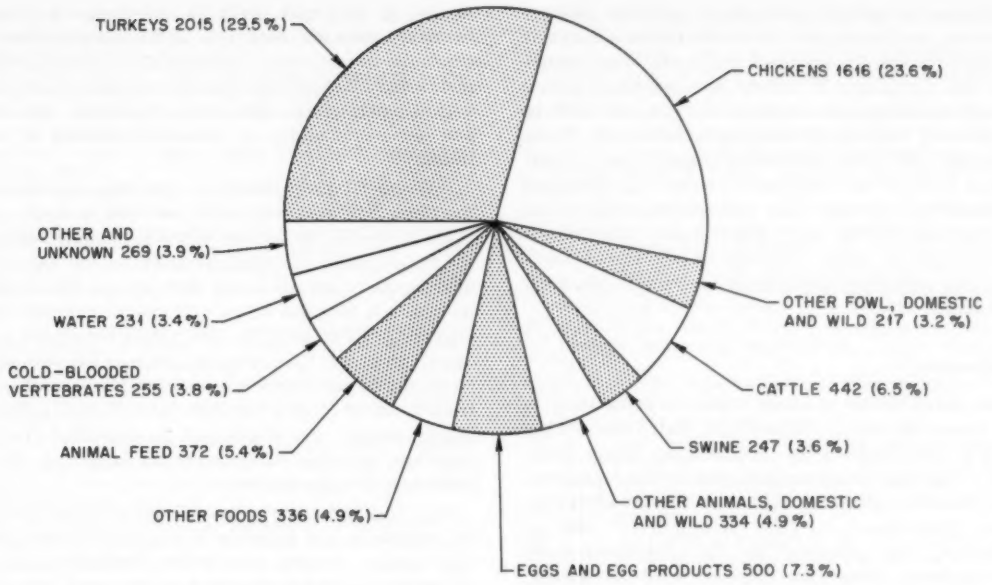
TURKEYS 2015 (29.5%)
CHICKENS 1616 (23.6%)
OTHER AND UNKNOWN 269 (3.9%)
WATER 231 (3.4%)
COLD-BLOODED VERTEBRATES 255 (3.8%)
ANIMAL FEED 372 (5.4%)
OTHER FOODS 336 (4.9%)
OTHER FOWL, DOMESTIC AND WILD 217 (3.2%)
CATTLE 442 (6.5%)
SWINE 247 (3.6%)
OTHER ANIMALS, DOMESTIC AND WILD 334 (4.9%)
EGGS AND EGG PRODUCTS 500 (7.3%)

Fig. 4 Number and percentage of nonhuman Salmonella *isolations from the indicated sources in the United States in 1965. At least 800 types of* Salmonella *have been isolated from animals.*

life to over 150 days at room temperature (25 to 28°C).

The shelf life of shrimp[45] at 0 to 4°C is extended from 3 days for unirradiated controls to 30 days by treatment with 150 krads and to 130 days by combining this dose with a mild heat-treatment. Storage at 10 to 12°C is extended to 65 days by irradiation and mild heat-treatment.

Table 4 EXTENSION OF REFRIGERATED SHELF LIFE BY IRRADIATION

Product	Radiation dose, krads	Shelf life, days	
		Normal	Irradiated
Canadian results			
Scallop meat	75	15	28 to 43
Haddock	75	12	25
Cooked lobster meat	75	14 to 21	28 to 35
Freshwater whitefish	150	11	29 to 35
U. S. results			
Shrimp	150	14 to 21	21 to 40
Crab	200	7	35
Haddock	200	12 to 14	30
Clams	400	5	30

Canadian Program

I do not propose to discuss the Canadian food-irradiation program in detail. Lillie[46] discussed our program at the Eleventh AECL Symposium on Atomic Power held at Toronto in October 1966, and various aspects of the program have been presented by MacQueen, Warland, and Ferguson[47–49] at international meetings held in Japan, Germany, and Poland in 1966.

The main highlight of our program, which was initiated in 1956, was the clearance for irradiated potatoes, received from the Food and Drug Directorate, Department of Health and Welfare, in 1960. This was the first clearance for any irradiated food in the Western World and was a significant breakthrough with regard to permitting the use of radiation as a method of preservation. The event had a stimulating effect not only on our Canadian program but also on programs conducted in other countries.

Throughout our 11-year program, we have worked closely with the responsible public health authorities in the Food and Drug Directorate to ensure that the plans we were making would tie in with their requirements for providing evidence on the safety of irradiated foods. We are fortunate in Canada to have the authority for clearing irradiated foods vested in a single agency, the Food and Drug Directorate, which is well staffed with competent scientists.

Radiation technology is well advanced and presents no barrier to future development in food irradiation. The AECL has demonstrated this fact by constructing a number of large-scale irradiators that have been operated successfully.

We anticipate that the results of our studies will be useful to investigators in developing countries. Additional research will be required in the countries

themselves on native foods since varieties, storage practices, packaging, and preirradiation handling may be quite different from those in Canada. Wholesomeness data (evidence on safety obtained from animal feeding experiments) obtained in Canada will be particularly valuable in developing countries. These expensive and time-consuming studies are an important part of the contribution which the developed countries can make. Our successful petitions on potatoes and onions have been widely distributed, and we plan to make available to developing countries our future petitions to assist them in obtaining clearances.

Conclusions

The possibilities of using radiation processing to help conserve and to improve the distribution of the world's food supplies are encouraging. Many countries, realizing the great potential of this technique, have initiated research programs. The 1966 International Symposium on Food Irradiation,[50] held at Karlsruhe, was attended by 200 scientists from 25 countries. Sixty-nine papers were presented, reporting the results of the various research programs, the majority of which are under way in developed countries. It was encouraging to note that some research programs had been initiated in developing countries, where the greatest benefits may be realized from this new technique. However, the real potential of food irradiation will not be realized unless more research programs are initiated and more people are trained in the associated disciplines.

In Canada we can make the greatest contribution to food irradiation by expanding our own research program, by providing developing countries with irradiators, and by offering them technical assistance to establish their own programs. The Canadian attitude on aid to developing nations was appropriately expressed by the Hon. Paul Martin, Secretary of State for External Affairs, in an address, "Canada and the World Economy," to the Vancouver Board of Trade on Jan. 18, 1967, in which he stated:

> Unless we place at the disposal of the less-developed countries some of the wealth of human and material resources which we possess, our own security cannot be assured. It is my personal conviction, which has been strengthened by years of experience in the field of foreign affairs, that aid constitutes one of the best and most constructive instruments we have in our quest for international peace and stability. Self-interest dictates that we should maximize our aid effort and improve the quality of our aid to the greatest possible extent. As the Minister responsible for external aid, I am proud of the fact — verified every day from the large number of verbal and written testimonies I receive — that it is humanitarian motives and an ingrained sense of social justice which are at the root of the widespread support which Canadians in all walks of life give to the national aid effort.

The solution of the problem of the world's hungry millions means that greater progress must be sustained in a broad field of activities — population control, education, research, agricultural production, economic development, and cooperation among governments and national and international agencies. Success will depend on the allocation of greater resources and the contributions of scientists working in many fields.

William Clark,[51] Director, Overseas Development Institute, has suggested that the total cost of a program to enable the peoples of the developing countries to double their personal incomes by the end of the century is modest. A net flow of capital of 1% of the national incomes of the developed countries would represent about half the cost. Other necessary steps are to improve the terms of trade of the developing countries by about 10%, increase their share of world trade from 26 to 28%, improve their foreign exchange requirements, and implement an extensive training program in order to increase the supply of skilled personnel 10% per annum.

Practical solutions to the problems of the developing countries are possible if man in a spirit of good will makes efficient use of the potential resources of nature and knowledge at his command. The next few decades will be critical in terms of increasing food supplies to serve the needs of increasing populations and of improving the diets of the millions suffering from malnutrition. With increasing support for research and training, we expect that the new technology of food irradiation could make a useful contribution to help alleviate those world food problems.

Perhaps the best approach to solving the world food problems is contained in the message expressed in the old proverb which states "Give a man a fish and he will eat for a day; teach a man to fish and he will eat for a lifetime." (MG)

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Radiation Preservation of Pacific Coast Fisheries Products*

By D. Miyauchi, J. Spinelli, G. Pelroy, and M. A. Steinbergt

Abstract: Results of experimental work at the U. S. Bureau of Commercial Fisheries Technological Laboratory, Seattle, during the last 5 years are presented. Irradiation of Northeast Pacific Ocean marine products with doses of 0.1 to 0.2 Mrad gives acceptable products with shelf life sufficient to allow marketing anywhere in the United States. Taste panels detected no significant difference between frozen fresh fish and irradiated fish stored 4 weeks in preference tests. Fish can be irradiated in retail packages or in large wholesale units. Some products require using oxygen-impermeable packaging materials and eliminating the air by vacuum packing or complete filling of the package to prevent oxidative rancidity. Helium atmosphere during irradiation gave effects similar to vacuum packing; nitrogen, air, and carbon dioxide atmospheres were detrimental. The effect of storage temperature on microflora is still being studied. Treatment with sodium tripolyphosphate helps retain original appearance and texture.

The Bureau of Commercial Fisheries Technological Laboratory in Seattle has been participating in a national program sponsored by the U. S. Atomic Energy Commission, Division of Isotopes Development, to develop procedures for preserving fishery products with low doses of ionizing radiation. The goal of this program is to advance radiation processing of selected seafood products to the point of commercialization, including clearance by the Food and Drug Administration. This article summarizes the results of experimental work completed at this laboratory during the last 5 years.[1-5]

Determination of Minimum Radiation Dose

In the preservation of seafoods with ionizing radiation, the minimum radiation dose that will extend the refrigerated, but unfrozen, storage life sufficiently to allow economical nationwide distribution of a uniformly high-quality product to the consumer must be used.[6] The advantages of using the minimum radiation dose are:

1. The product differs least in appearance, odor, and flavor from the original fresh fish or shellfish.
2. The storage life of the product will be terminated by bacterial spoilage before degradation in flavor and texture from other causes, e.g., enzymatic spoilage, becomes a major factor.
3. The cost of irradiation per pound of product is kept at a minimum.

Fresh fish of highest quality and good methods of handling the fish must be used; this results in an even higher quality finished product.

Species Studied

To operate economically, a radiation facility for processing fish requires a large throughput to keep processing costs at a low level. Enough fishery products that can be successfully irradiated are needed to level out seasonal fluctuations in production and to respond to changes in market demands. This study emphasized fin fish—petrale sole, English sole, Pacific ocean perch, and halibut. During the winter months, when the catch of fin fish is low, production of Dungeness crab and Pacific oysters is high; so these species were included in the study.

Storage Studies

Radiation-pasteurized marine products can be marketed in several different ways. For example, the product may be packed in the retail package, irradiated, and distributed, to be removed from the package by the consumer only. The product may also be packed in large wholesale units, irradiated, dis-

*Responsibility for management of AEC's Food-Irradiation Program is divided between the Division of Isotopes Development and the Division of Biology and Medicine. The findings reported in this article are the result of investigations conducted under Division of Isotopes Development contracts.

†U. S. Bureau of Commercial Fisheries Technological Laboratory, Seattle, Wash.

tributed, and repackaged by the distributor or retailer before being sold to the consumer. This study included both methods.

PRODUCTS PACKED IN RETAIL PACKAGES

Packaging halibut steaks[4] and fillets of petrale sole,[7] English sole,[4] and Pacific ocean perch[5] in oxygen-impermeable material and eliminating the air from the package gave irradiated products with the best storage characteristics. The fish were packed in cans or heat-sealable polyester pouches. Air adjacent to the fatty tissue of the fish caused discoloration and the development of rancid odors and flavors within 1 to 2 weeks of storage at 33° F. With Dungeness[8] and king[9] crab meats, air packing or vacuum packing in cans or heat-sealable polyester pouches was generally suitable. For oysters, jars with screw-cap lids and cans—the containers used commercially for marketing fresh oysters—were used.

A radiation dose in the range 0.1 to 0.2 Mrad was sufficient to give irradiated seafoods a shelf life of 2 to 5 weeks at 33° F. This is 2 to 5 times as long as the corresponding control samples (Table 1). Thus

Table 1 COMPARISON OF SHELF LIFE OF IRRADIATED AND NONIRRADIATED PACIFIC COAST FISHERY PRODUCTS

Product	Dose, Mrad	Shelf life, days	
		At 33°F	At 42°F
Petrale sole fillets	None	4–11	3–7
	0.1–0.15	20–25	3–8
	0.2	21–42	12–18
English sole fillets	None	4–6	-
	0.1	14–21	-
	0.2	21–28	-
Pacific ocean perch fillets	None	6–7	-
	0.15–0.2	25–28	-
Halibut steaks	None	4–18	<4–8
	0.1	14–21	-
	0.2	21–56	14–21
Dungeness crab meat	None	6–14	2–9
	0.1	14–35	14–21
	0.2	21–56	21
King crab meat	None	5–14	3–7
	0.1	21	7–14
	0.2	28–42	14
Pacific oysters	None	20	9
	0.1	30	11
	0.2	30–34	20–25

irradiation of Northeast Pacific Ocean marine products with doses of 0.1 to 0.2 Mrad produces highly acceptable products having a shelf life adequate to allow marketing throughout the country. The results also indicate that the radiation dose can be varied within a 0.1- to 0.4-Mrad range, as the requirements for commercial application of the process become apparent, without greatly affecting the acceptability of the product.

PRODUCTS PACKED IN LARGE WHOLESALE UNITS

Fish processors in Oregon and Washington pack fresh fish fillets in polyethylene bags, usually 25 lb per bag, for the institutional and wholesale market. The bags of fillets are iced and shipped by truck or railroad to the marketing area. The short and variable shelf life of these fillets—from 4 to 7 days—has limited the marketing of fresh fish to regions near processing centers. By irradiating fishery products with low doses, the processor can increase shelf life sufficiently to ship fish into more distant marketing areas.

Experimental results,[5] given in Table 2, indicate that English sole fillets packed in large polyethylene bags or heat-sealable polyester bags and irradiated at 0.2 Mrad can be held 2 weeks at 33° F. They can then be repacked into retail packages and be held for an additional 5 days, which is the shelf life of the nonirradiated control samples. Thus 2 weeks of additional storage was gained by low-dose radiation processing.

Results with Pacific ocean perch fillets were equally promising. With halibut, results were best using pieces of halibut vacuum packed in cans or in heat-sealable polyester bags before being irradiated. Dungeness crab meat irradiated in size No. 10 cans, the container used commercially for marketing fresh crab meat, was held as long as 20 days before being repackaged into retail packages.

In current studies, fillets of English sole, petrale sole, and Pacific ocean perch have been packed in 10- and 20-lb units, irradiated at 0.2 Mrad, and shipped by regular commercial carrier to fish buyers in various parts of the country. In all shipments the irradiated fillets were superior in quality to, and had a storage life 2 to 3 times as great as, the nonirradiated controls.

Preference Tests on Radiation-Pasteurized Seafoods

The benefits derived from treating various fishery products with low doses of ionizing radiation—namely, maintaining higher product quality and extending shelf life—have been conclusively demonstrated in laboratory tests and in shipping tests made through regular commercial channels. However, before radiation processing of fishery products can be commercialized, the consumer has to accept the irradiated product. To gain data that would help indicate the probable acceptability of the irradiated product, preference tests were conducted using a panel of Bureau of Commercial Fisheries employees.[3,4,10]

Samples of nonirradiated and irradiated petrale sole fillets, halibut, and Dungeness and king crab meats were prepared from the same lots of fish. The nonirradiated samples were frozen and stored

Table 2 SHELF LIFE OF SEAFOODS IRRADIATED IN WHOLESALE UNITS, STORED, AND REPACKAGED

Product	Package*	Dose, Mrad	Initial storage, days	Shelf life, days, after repackaging†	Shelf life of nonirradiated control, days†
English sole fillets	Polyethylene or polyester bag	0.2	7	9	5
		0.2	14	5	5
Pacific ocean perch fillets	Polyethylene or polyester bag	0.2	7	7–11	4–7
	Polyethylene bag or poly tin	0.2	10	9–13	4–7
	Polyethylene bag, poly tin, or polyester bag	0.2	14	3–8	4–7
Halibut pieces	Polyester bag or No. 10 can	0.25	14	7–9	5–14
		0.25	21	7	5–14
Dungeness crab meat	No. 10 can	0.2	12	5–7	7–12
		0.2	20	3–6	7–12

*Polyethylene bag: 14 by 28.75 in., 2.75 mils thick; polyester bag: 16 by 30 in., 4 mils thick, heat-sealable; poly tin: fillet can, 15 by 10.5 by 4.5 in. high, lined with 2-mil-thick polyethylene bag.
†Packed in paperboard tray with a cellophane overwrap.

at −20° F; the other samples were irradiated at either 0.2 or 0.25 Mrad and stored at 33° F. After 2 and 4 weeks of storage, the irradiated and nonirradiated samples were prepared by various recipes and presented to the taste panel for preference rating (Table 3). No significant difference was found, at the 95% confidence level, between the fresh frozen samples and the irradiated samples stored for either 2 or 4 weeks.

Petrale sole fillets were also tested by the Army at Fort Lee, Va.,[3] to determine the comparative acceptability of irradiated and fresh frozen samples served as part of a normal meal under garrison feeding conditions. After irradiated fillets were held at 33 to 35° F for 16 and 28 days, they were breaded and deep-fat fried. The irradiated fillets were served to 158 participants; the nonirradiated control samples were fed to 175 participants. For the 16- and the 28-day samples, the mean hedonic scores (see Table 3) were 5.90 and 6.52, respectively; those for the frozen fish were 6.43 and 6.57. Statistical analysis of the mean scores showed a significant difference between the mean scores at the 95% confidence level for the 16-day sample but not for the 28-day sample. Although the ratings for the nonirradiated fish were generally higher than for the irradiated, the irradiated product was highly acceptable to the test participants.

The results of these limited preference tests on irradiated Pacific marine products indicate good consumer acceptance and suggest the consideration of test-marketing studies on a larger scale.

Studies on Processing Variables

EFFECT OF ATMOSPHERE IN THE PACKAGE

Some fish and shellfish—notably haddock, shrimp, and Dungeness and king crab—lend themselves to irradiation with air in the package, but sole and flounder fillets irradiated this way become rancid after 10 to 14 days of refrigerated storage. These oxidative changes occur primarily in the fatty layer along the lateral line and on the edges of the fillets exposed to the air in the package. They can be prevented by using oxygen-impermeable packaging materials and eliminating the air by vacuum packing or by complete filling of the package. Of the various experimental packs tried, vacuum packing fish fillets in cans for irradiation gave the best results.

Several investigators who have studied the role of air in causing rancidity in irradiated lipids think that

Table 3 MEAN PREFERENCE SCORES OF IRRADIATED AND NONIRRADIATED SEAFOODS

Product	Number of judges in panel	Storage time, weeks	Dose, Mrad	Mean preference score*	
				Nonirradiated, stored at −20°F	Irradiated, stored at 33°F
Deep-fat-fried petrale sole fillets	50	2	0.2	7.68	7.52
	53	4	0.2	7.49	7.32
Deep-fat-fried halibut	43	2	0.25	7.60	7.72
	46	4	0.25	7.59	7.33
Baked halibut	30	2	0.25	7.17	7.13
	32	4	0.25	7.16	7.34
King crab meat cocktail	43	2	0.2	7.23	7.14
	47	4	0.2	6.93	7.47
Dungeness crab meat cocktail	55	2	0.2	7.14	7.23
Dungeness crab meat salad	63	2	0.2	7.33	7.44
Dungeness crab meat rice casserole	63	2	0.2	7.76	7.46

*Based on a 9-point hedonic scale where 1 to 4 indicate degrees of "dislike," 5 indicates neither like nor dislike, and 6 to 9 indicate degrees of "like."

the formation of ozone during irradiation starts many undesirable reactions. Tests at this laboratory have shown that severe rancidity can be produced in less than 3 days after sole fillets are exposed to small quantities of ozone.

To test the effect of atmosphere during irradiation, fish fillets were irradiated in nitrogen, carbon dioxide, and helium.[4] Only helium gave results that were comparable with vacuum packing. Nitrogen and carbon dioxide offered no protection to the irradiated product. Nitrogen is not an inert atmosphere in the presence of gamma rays, and the radiolysis products of nitrogen and water vapor react with fish substrates to initiate reactions that ultimately result in flavor deterioration.

EFFECT OF STORAGE CONDITIONS ON THE MICROFLORA OF IRRADIATED FISH

Postirradiation storage variables, such as the kind of gas in the package and the temperature, can have as much effect on the composition of the spoilage flora as the radiation treatment itself. The spoilage flora of petrale sole fillets that had been vacuum packed in cans were predominantly *Lactobacillus*,[11] a microorganism also found in vacuum-packed luncheon meat. The spoilage flora of irradiated fillets stored in oxygen-permeable films consisted of *Achromobacter* and *Trichosporon* yeasts.[12] *Pseudomonas* predominated in the nonirradiated fish stored in either type of package.

The storage atmosphere had a dramatic effect on the yeast microflora of irradiated king and Dungeness crab.[13,14] The yeasts multiplied in the air-packed samples but were almost completely suppressed in the vacuum-packed samples. Genera isolated from irradiated crab meat included *Trichosporon, Cryptococcus, Rhodotorula, Pullularia, Candida,* and *Torulopsis.*

Storage temperature is a critical factor in controlling microbial populations. Refrigeration storage temperatures inhibit the growth of bacteria that might be considered a hazard to public health, but certain psychrophilic spoilage organisms are able to survive and grow well at the same low temperature. Because radiation-pasteurized seafoods, like other perishable foods, can be mishandled, whether or not these seafood products become completely unacceptable as a result of deteriorated physical appearance and spoilage off-odors before they might become a health hazard must be determined. A study is in progress to determine the effect of storage temperature on the composition of the microflora of irradiated and nonirradiated petrale sole fillets and to determine the outgrowth of aerobic organisms that are potentially a public health hazard, such as fecal coliforms, coagulase-positive *Staphylococcus aureus,* and enterococci. The results so far indicate that irradiation suppresses the growth of most of these organisms. No *Staphylococcus aureus* and very few enterococci have been found in irradiated fish at any storage temperature. Coliform organisms did grow at storage temperatures above 42° F in nonirradiated fish. The predominant spoilage organism of irradiated fish at all storage temperatures was *Lactobacillus.* The predominant spoilage organism in nonirradiated fish stored below 42° F was *Pseudomonas.*[15]

TREATMENT WITH SODIUM TRIPOLYPHOSPHATE

Although low-dose irradiation delays gross changes in quality by destroying a large part of the bacterial population, other changes occur during storage which affect the quality and appearance of the irradiated product but are not associated with microbiological growth. These changes include loss of drip, alteration in color, alteration in texture, and some loss of flavor. The extent to which these changes adversely affect the quality of the irradiated product depends largely on the species of fish and the length of time the product has been held in storage.

Treating fillets prior to irradiation by dipping them in sodium tripolyphosphate–salt solutions of appropriate concentrations (7.5% sodium tripolyphosphate and 2% sodium chloride) is compatible with radiation pasteurization[16] and is effective in minimizing drip during storage. This treatment also helps retain the original appearance and texture, particularly with such species as halibut and Pacific ocean perch. Dipping does not affect the odor or flavor of the product. No significant differences were found in the spoilage flora between phosphate-treated and untreated vacuum-packed fillets.

Microbial Spoilage of Irradiated Fish

The growth of microorganisms is the major cause of spoilage of fresh fish. The predominant spoilage organisms of nonirradiated fish are *Pseudomonas,* which grow at low temperatures. Subjecting fish to low doses of ionizing radiation preserves fish because the radiation destroys or inactivates nearly all of these microorganisms.

In earlier work with king crab meat, significant quantitative differences in the bacterial populations of nonirradiated and irradiated samples at the time of spoilage were found.[6,17] The nonirradiated samples were usually judged to be unacceptable in quality when the bacterial counts exceeded 10^6 per gram, while the irradiated samples were seldom considered to be spoiled until the bacterial counts approached 10^8 per gram. A similar pattern was observed in studies on petrale sole. In addition, the off-odors and flavors associated with spoilage of the nonirradiated products were different from those of the irradiated products.

Irradiation causes a qualitative change in the microflora because some groups of organisms are more resistant to radiation than others. These qualitative differences in the microflora cause odors found

in irradiated products to be different from those of the nonirradiated product.

Representatives of the various microbial groups were studied in detail to determine which of their biochemical activities might lower the quality of the product. The *Trichosporon* yeasts, which were the predominant spoilage organisms in air-packed irradiated crab and fillets, were found to produce lipolytic and proteolytic enzymes.[14,18] The *Pseudomonas* organisms, which cause the spoilage of nonirradiated fish, produced various hydrolytic enzymes that are known to produce malodorous breakdown products in foods. The *Lactobacillus*, which spoil vacuum-packed irradiated fish and other vacuum-packed products, were acid producers but produced no proteolytic or lipolytic enzymes.[3]

The spoilage pattern of radiation-pasteurized fish muscle inoculated with pure cultures of these microorganisms was studied under both aerobic and anaerobic conditions. Sensory and chemical analyses[5] showed that the spoilage produced by *Pseudomonas* was characterized by putrefactive and ammoniacal odors. *Achromobacter* produced sweet or watermelon-like odors at incipient spoilage; these became nauseous and ammoniacal as spoilage progressed. *Lactobacillus* produced stale and sour odors, and the *Trichosporon* yeasts produced yeasty odors.

Some of the unusual odors that have been observed in spoiling, irradiated fish therefore can be attributed to particular microorganisms. The results of chemical determinations also correlate with the enzymatic activity of these organisms.

Assessment of Quality of Irradiated Fish

The quality of radiation-pasteurized fish decreases in steps. The general pattern of sensory changes occurring in fish stored at 33° F after irradiation at 0.2 Mrad and the numbered tests that detect the steps in the process are shown in Fig. 1. Quality changes in the irradiated fish are rapid in the early and the terminal phases of storage. Early quality changes that are reflected primarily by loss of flavor are caused by autolytic processes and can be correlated with the degradation of inosine monophosphate (IMP) and the accumulation of hypoxanthine.[19–21]

Except for textural alteration that appears to correlate with alteration of the myofibrillar protein, flavor and odor are rather stable until bacterial counts approach 10^7 per gram. The amount of volatile acids that accumulates in the tissue shows good correlation with these latter sensory changes. Trimethylamine, depending on the dose, can also be related to sensory change.[8,17] In the terminal phase of storage, bacterial counts approach 10^8 per gram; volatile acid number exceeds 20, and about 75% of the free glucose originally present in the tissue has been consumed. Histamine, low-molecular-weight carbonyls, and free ribose show only slight changes during normal storage and bear little if any relation to the quality of the irradiated fish. Thiobarbituric acid numbers determined on whole fish do not accurately reflect the development of rancidity in irradiated fish.

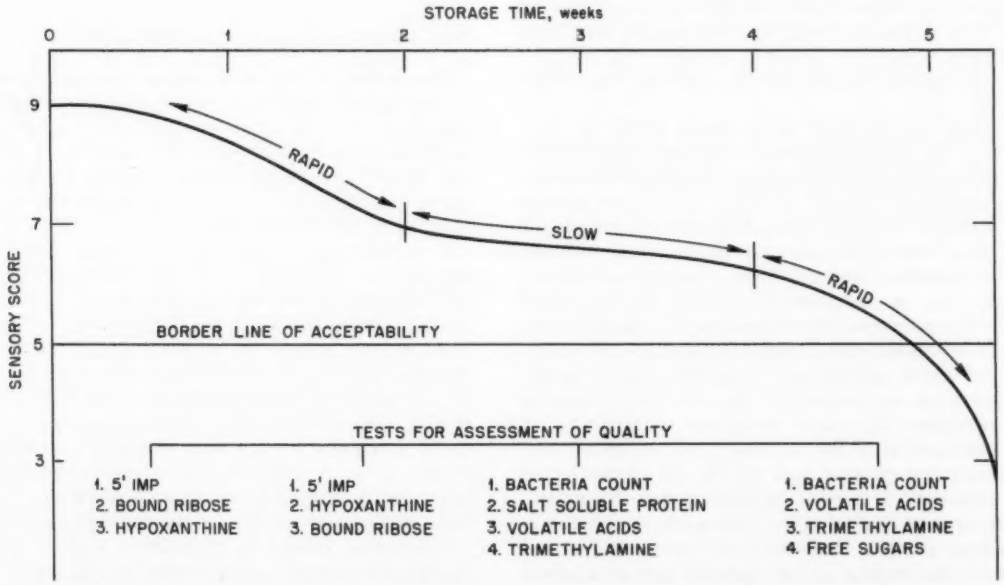

Fig. 1 The pattern of sensory changes that usually occur in fish irradiated at 0.2 Mrad and stored at 33°F. Indicated are the objective tests that best correlate with these changes.

Conclusion

After 5 years of study of radiation pasteurization of fish, minimum dose has been established for the various fin fish studied, and a product that should be commercially acceptable has been achieved. Studies of the microflora and radiolysis of irradiated fish indicate that few, if any, serious problems remain to be solved. Consideration should now be given to large-scale shipping and marketing studies. (FEM)

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Section

IV

Isotopes and Radiation Technology

Process Radiation Development

The First Industrial Gamma-Irradiation Plant on the European Continent*

By A. Künzli and P. Baur

Abstract: The Braun Company's ^{60}Co medical-supply sterilization plant (600 thousand curies capacity) in Melsungen, West Germany, is described.

In 1964 the firm of B. Braun, makers of surgical and pharmaceutical products in Melsungen, West Germany, decided to build a gamma-irradiation plant. This first industrial-scale plant on the European Continent was both planned and installed by Sulzer Brothers Limited of Winterthur, Switzerland. The plant is designed for a ^{60}Co source of 600 thousand curies and provides for automatic sterilization of all kinds of medical products.

Plant Layout and Mode of Operation

The plant (Fig. 1) is divided into the preparation room (Fig. 2), the irradiation cell, and the crane hall with the two loading wells (Fig. 3). The preparation room is in the form of a basement, accessible from the adjoining production building. The preparation room communicates with the cell through a feeding labyrinth and an access opening. Access to the crane hall is either from outside, through the door at ground level, or from the preparation room, through the loading wells.

In the preparation room the various packaged materials are loaded into the irradiation containers. Via a horizontal conveyor, a batching device, and a lifting device, these containers pass through a labyrinth into the irradiation cell. Here they are pushed from the horizontal conveyor onto a vertical conveyor by a charging device and carried past the radiation source several times. Thus the material is brought into every possible position relative to the source, ensuring very small variation of the dose inside the packages. From the vertical conveyor (Fig. 4), the material passes along a sloping roller conveyor through a second labyrinth and back into the preparation room.

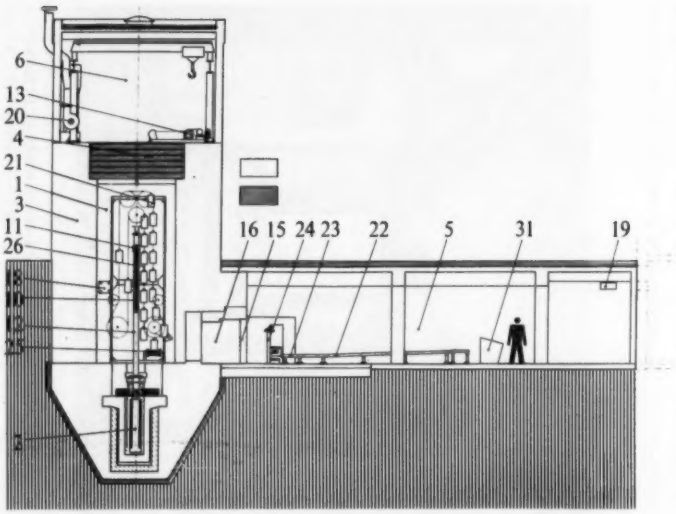
Apart from filling and emptying of the irradiation containers in the preparation room, the whole feeding and irradiation sequence takes place automatically. During plant operation, personnel are present only in the preparation room. The other rooms may also be entered for inspections and maintenance work and for charging and discharging the source carrier.

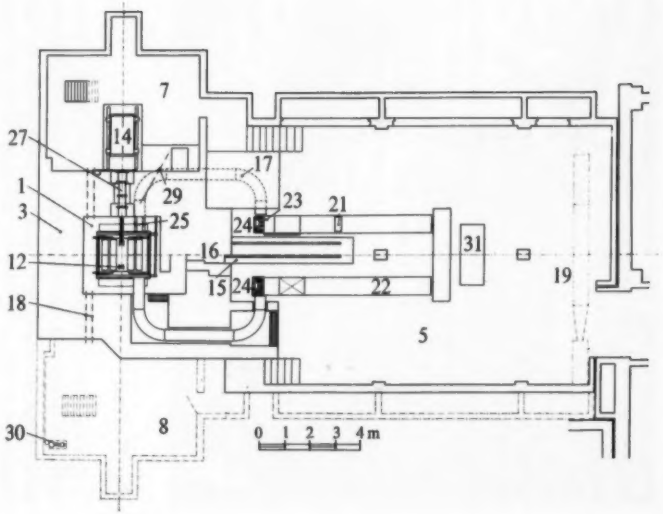
Shielding and Radiation Monitoring

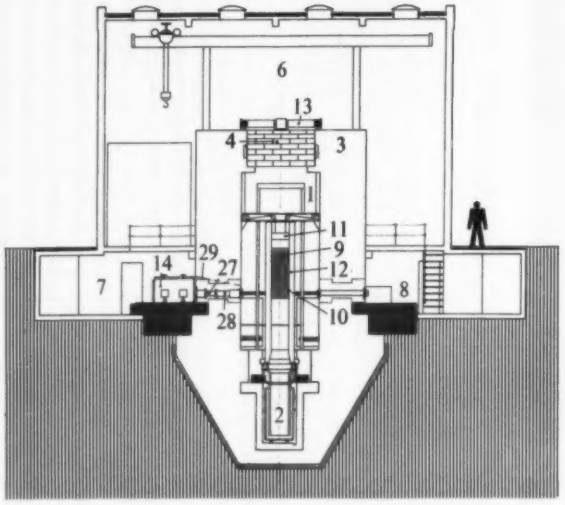
The cell walls are of ordinary concrete. In the cell roof is an opening covered with self-supporting dense concrete beams. Concrete of higher densities was used at some points. As far as possible, openings through the shielding are in the form of baffles, involving one or more changes of direction. This is the case with the passages between the preparation room and the irradiation cell, with the openings for the cables suspending the source carrier, and with the electrical leads and ventilation ducts.

The opening between the preparation room and the irradiation cell is closed by a door on rollers. Between the cell and each of the two loading wells are four openings, passing straight through and lined with steel tubes but normally sealed off with plugs. After provision of additional shielding, it is possible in emergencies to perform manipulations through these openings from the outside. When maintenance work must be done in the irradiation cell, the source is lowered into the pit; the cell is shielded from the source by a plug bolted to the source carrier. The inner walls of the concrete pit are lined with steel plate. Any water accumulating here can be drawn off by the self-priming motor-driven pumps (installed in the loading wells) and checked for radioactivity.

*Reprinted, by permission and with minor editorial changes, from *Sulzer Technical Review*, 48(2): 84-87 (1966).







1 IRRADIATION CELL
2 SOURCE PIT
3 CELL WALL
4 CELL ROOF
5 PREPARATION ROOM
6 CRANE HALL
7 RIGHT–HAND LOADING WELL
8 LEFT–HAND LOADING WELL
9 SOURCE ELEMENT
10 SOURCE CARRIER
11 SHIELDING PLUG ABOVE SOURCE CARRIER
12 SOURCE GUIDING RAILS
13 SOURCE LIFTING GEAR
14 SOURCE TRANSPORT CONTAINER
15 CELL ACCESS OPENING
16 DOOR ON ROLLERS
17 FEEDING LABYRINTH
18 RESERVE OPENINGS
19 AIR SUPPLY PLANT
20 AIR EXHAUST FAN
21 IRRADIATION CONTAINER
22 HORIZONTAL CONVEYOR
23 BATCHING DEVICE
24 LIFTING DEVICE
25 CHARGING DEVICE
26 VERTICAL CONVEYOR
27 CHARGING PASSAGE
28 REVOLVING PLUG
29 WINDOW
30 MOTOR–DRIVEN PUMP
31 CONTROL CONSOLE

Fig. 1 Elevation and plan of ^{60}Co irradiation facility.

Fig. 2 Preparation room.

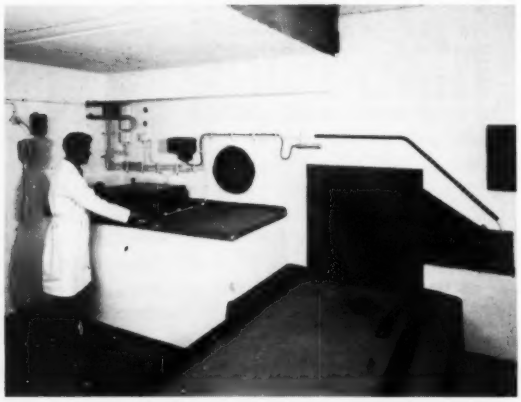


Fig. 3 Right-hand loading well.

The radiation level is monitored continuously in the preparation room, crane hall, and loading wells. If a threshold value, adjustable for each measuring zone, is exceeded, warning lights are switched on and an acoustic signal is given at the same time.

Radiation Source

The radiation source consists of ^{60}Co rods welded gastight in a tube of stainless steel. A source element is formed by 24 of these rods welded into an outer tube of stainless steel.

The source carrier (Fig. 5) has 77 horizontal channels arranged in two parallel vertical planes. A source element can be pushed into each of these channels. Suspended from two wire cables, the source carrier occupies the middle of the irradiation cell in its working position. The gear for raising and lowering the source is located above the cell roof. Rails fixed to the two narrow sides to guide the source carrier also prevent elements from dropping out. The elements are supplied in a shielded transport container. Before insertion of an element, the appropriate channel of the source carrier is positioned at the height of the charging passage. Exact adjustment is facilitated by observation of the cell from the loading well through the radiation-shielded window. The outer part of the charging passage consists of a revolving plug with a hole through it at an angle to the axis of rotation and capable of being aligned on the appropriate source-carrier row. The transport container is joined directly to its outer end. This arrangement enables all lattice spaces to be loaded in both planes of the source carrier from a single position of the transport container. If any difficulties arise when the source carrier is being loaded, the source element can be pushed back into the transport container from the left-hand loading well, using the push rods provided.

Ventilation

The ventilation plant supplies the preparation room with fresh air and extracts the heat liberated by the absorption of nuclear radiation. Supply air for the preparation room is drawn through a filter, from outside, by a fan and then passes through the feeding labyrinth into the irradiation cell. Air is exhausted by one of the two fans—the other acting as a standby unit—through a filter, leaving the building via an air exhaust duct. The air flow delivered by the fan is sufficient to extract the heat generated by the source

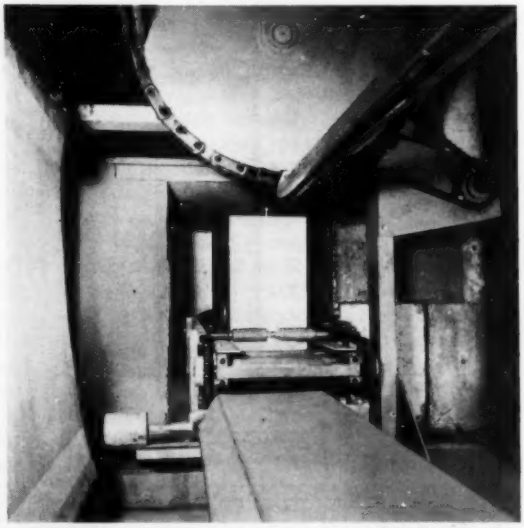


Fig. 4 Charging device and carrier rail of vertical conveyor.

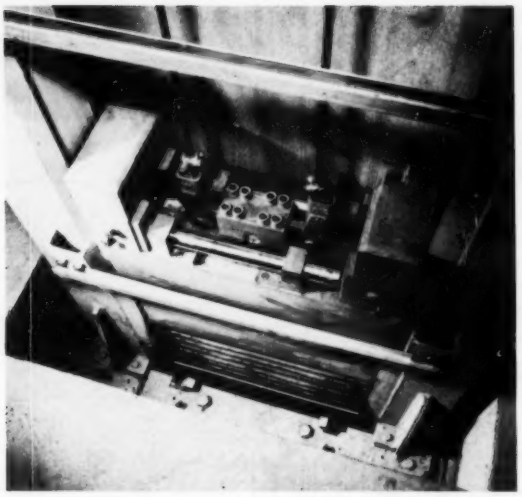


Fig. 5 Source carrier and pit.

and to keep at a low concentration the ozone resulting from irradiation of air. Part of the air flow provides constant cooling of the source pit. When the source is lowered, automatically controlled flaps divert the main flow through the source pit, leaving the remainder of the air flow to pass through the cell.

Control and Safety Interlocks

All electrical controls and instruments are housed in the control desk. To put the plant into operation, a switch must be operated and the "Source Open" button pressed. When the source has completed half its travel, the various motors of the conveying system automatically begin to run in the prescribed sequence. The conveying speed can be varied continuously by time switches. The sequence of operations can be followed on an illuminated diagram. Any faults are signaled automatically by illuminated indicators. When the switch is set at "Checking," all motors can be operated singly. In case of a current failure, the whole plant is supplied from an emergency generating set.

Numerous mechanical and electrical interlocks prevent exposure of personnel to harmful radiation due to incorrect manipulations. The electrical control system is designed on the "fail-safe" principle. In the event of power failure or excessive temperature in the irradiation cell, the source carrier automatically drops into the pit under its own weight. If one of the air exhaust fans should fail, a flow detector causes the standby fan to be switched on at once. In order to assist an ascending air flow if both fans should fail as a result of a breakdown of both normal and emergency electricity supplies, the fans and all connecting butterfly valves are paralleled by a bypass duct that opens automatically. (MG)

Traveling Exhibit on Uses of Irradiation Techniques*

As part of its responsibility for promoting the use of isotopes and radiation in European Atomic Energy Community countries, the Euratom Eurisotop Bureau is preparing a campaign to demonstrate industrial applications of irradiation techniques. This is being referred to as the IRAD campaign. In it the IRMA mobile irradiation facility, with its 1.75×10^6-curie ^{137}Cs source, will stop at various towns, where industries and research laboratories may use it.

Before the start of the tour, a questionnaire was sent to a number of firms, asking for data on the firm and including a list of possible irradiation applications. Applications mentioned included textile fiber grafting to improve dyeing and heat resistance, polymer production, medical products sterilization, food preservation, and insect elimination by the sterile-male technique. The industries contacted were asked to supply material that might be irradiated as part of a demonstration.

The IRMA irradiator (Fig. 1) is transported on a trailer truck (Fig. 2). The irradiation chamber, which is 80 by 80 by 160 cm, is shielded with 15 cm of lead. The radiation source, a rack of ^{137}Cs rods, is housed in an adjacent compartment when not in use. Products to be irradiated are placed in a series of 30- by 30- by 60-cm aluminum containers, which are conveyed around the source in such a way that each face of each container is exposed, one after the other, to the source, ensuring a homogeneous radiation dose. The containers enter and leave the irradiation chamber through a cylindrical port that is divided into four cells by lead walls. This arrangement provides biological shielding as the port is rotated to bring the product containers to the in-cell conveyor. The conveyor system has a capacity of 22 containers.

*Based on personal communications from G. Pröpstl of Eurisotop Bureau, Brussels.

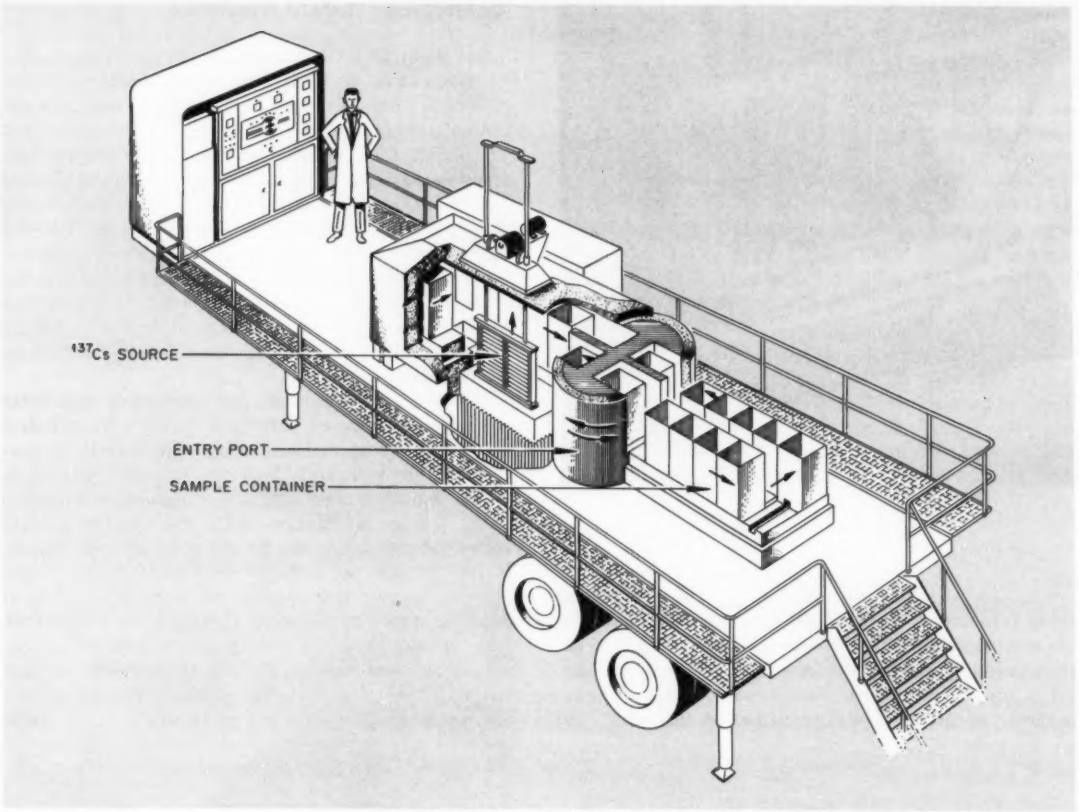


Fig. 1 IRMA mobile ^{137}Cs irradiator.

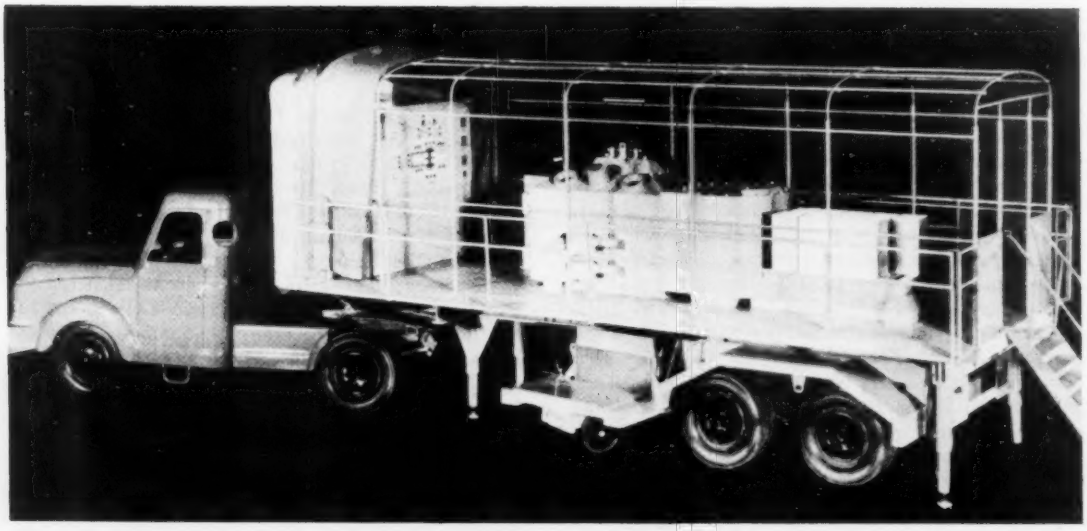


Fig. 2 IRMA irradiation facility on its truck.

The irradiator can process, per hour, 200 kg of fish with a "pasteurizing" dose of 0.3 Mrad; 30 to 60 kg of wood plastic, which requires a dose of 1 to 2 Mrads; or 10 to 15 kg of catgut with a sterilizing dose of 2.5 Mrads. When the total dose required is less than 0.3 Mrad, a single pass is used. For higher doses a multipass schedule is used, with the containers passing the source in a "carousel" formation until the required dose has been administered.

(Martha Gerrard)

NEW ^{60}Co IRRADIATOR

Availability of the Gammabeam 650 irradiator was announced recently by the Commercial Products division of Atomic Energy of Canada Limited. The chief features claimed by the company are versatility, reliability, and low cost. Designed for use in a shielded room, with a 30-thousand-curie source it can make panoramic irradiations at a dose rate of 2.4×10^4 r/hr or irradiations inside the annular source at dose rates from 1.8×10^5 to 5.4×10^6 r/hr. The price ranges from $37,700 with 5 thousand curies of ^{60}Co to $50,200 with 30 thousand curies. (MG)

USE OF ISOTOPES IN MEDICINE (in French)
By A. G. Frêre (Medical Director of the Clinique Cesar De Paepe, Brussels),
Editions Arscia S. A., Brussels, 1966,
72 pp. plus 48 plates and 29 references, $11.50

The theory on which diagnosis by means of radioisotopes is based and procedures for carrying out the diagnosis are described for thyroid, blood and hematopoietic organs, heart, kidney, and brain. Some of the newer isotopes — e.g., ^{125}I, ^{99m}Tc, and ^{197}Hg — are included. The book is designed for the practicing physician, not the technician, and the French is not too difficult. The 34 scintigraphs in color and 14 black-and-white photoscans are interesting even to those who know no French. (MG)

Section V

Isotopes and Radiation Technology

Isotopic Power Development

Radioisotope-Powered Submersible Engine

Abstract: A conceptual design for a RadioIsotope Submersible Engine (RISE) is presented. This unit, which is designed to produce 3 kw(e) for 10 thousand hr, is powered by 1.59 Mc of ^{60}Co. It operates on a dynamic closed Rankine cycle with Dowtherm A as the working liquid. With suitable modifications the design can produce 2 to 20 kw(e).

Future interest in the exploration and utilization of the ocean will necessarily be based on the development of a wide range of special devices and equipment. Many characteristics of this equipment are still undefined; however, a self-contained power supply capable of operating submerged for an extended time is essential to the performance of most missions of interest in oceanography. Conventional power sources have relatively limited life; and nuclear reactors are applicable to high power-level requirements but are relatively large and expensive for levels <100 kw(e). A compact radioisotope engine, however, would be suitable for a variety of applications[1,2] requiring a power level of a few kilowatts. Applications would include power for propulsion of small submersibles, power for manned underwater platforms, and power for a variety of unmanned underwater platforms.

Aerojet-General Nucleonics, under a contract with the Division of Isotopes Development, AEC, has developed a conceptual design for a radioisotope-powered engine, with a power range of 2 to 20 kw(e) for a small submarine. The major goal was design of a power plant that demonstrates all important concepts to be used in a family of radioisotope engines covering various power levels and applications. The design, which has been covered in great detail in a number of reports,[3–6] is described briefly here. This conceptual design was to provide information for a demonstration model of the RadioIsotope Submersible Engine (RISE) in sufficient detail to permit (1) realistic evaluation of the potential of the system, (2) detailed planning of component and system development and testing, and (3) identification of potential problem areas. Although a schedule was proposed[7] in 1965 to construct a working model from the conceptual design, construction has not been started to date. However, the AEC has requested proposals on design and fabrication of a heat-source demonstration unit utilizing 2 Mc of ^{60}Co. This heat source could provide technology and proof-of-principle for power-conversion units.

General contract constraints included (1) maximum use of available technology so as to ensure a workable system in a minimum time, i.e., the early 1970's, and (2) a design suitable, without major modifications, for a wide range of power outputs.

The RISE demonstration system consists of a boiler fueled with ^{60}Co coupled directly to a Dowtherm A* Rankine-cycle power-conversion system. The radioisotope heat source consists of nickel-plated ^{60}Co disks encapsulated to form pins which are arranged in a hexagonal array in the center of the boiler. The Dowtherm A Rankine-cycle power-conversion system was selected on the basis of a separate study. Provision has been made in the design for normal, standby, and a fail-safe cooling system. The designed unit would be about 24 in. in diameter and 90 in. high.

In the description that follows, developments of design criterions for the total system, for the ^{60}Co heat source, and for the power-conversion system are discussed.

System Design Criterions

The overall objective of the RISE system is to provide radioisotope power for a wide range of undersea applications. The specific design criterions for the power plant were to be developed as a part of the contract; the general criterions related to the overall system include:

1. The cost of the system should be low, as this is the only way many potential applications will materialize.

2. The fueling and maintenance intervals should be long, thus giving radioisotope systems an advantage over chemically fueled systems.

*Dowtherm A is a eutectic mixture of diphenyl and diphenyl oxide. It melts at 53° F and has a vapor pressure of 107 psia at 700° F.

3. Any radioisotope fuel should be absolutely contained because of the nature of the marine environment. Containment can be assured if two conditions are met: (1) provision for safe removal of unused radioisotope heat under all credible circumstances to avoid meltdown and subsequent release of fuel; (2) provision for long-term resistance to corrosion by seawater.

Criterions more directly related to this specific demonstration program include:

1. The design should be suitable for the power-level range of 2 to 20 kw(e).

2. The power plant should operate for 10 thousand hr without servicing.

3. High overall thermodynamic efficiency should be achieved. Thermodynamic efficiency affects the needed radioisotope fuel inventory, which directly influences the power-plant cost, and, in turn, the system weight, which is affected by the bulk of shielding required for the fuel.

4. System weight should be minimum since power-plant weight is critical for some applications, such as for small submarines with limited buoyancy. Low weight also simplifies handling problems in transporting, placing, and recovering fixed systems.

5. Minimum orientation sensitivity is desirable. Some potential missions may require a power plant that will operate in a variety of positions. Specifications for equipment for combat submarines call for operation at ±30° of design trim. Similar allowable misorientation will probably be needed for small submersibles. Some allowable power-plant misorientation may also be needed for static systems, particularly during placement.

6. The power plant must withstand ambient seawater pressure, which determines depth capability. For the demonstration program all power-plant components will be packaged within a pressure vessel.

7. Low noise is a general requirement to avoid limiting the applications of RISE. Many hydrospace applications involve the use of acoustic devices since sound is one of the few forms of energy that can be transmitted efficiently through seawater.

8. The demonstration unit is to incorporate conservative shielding. Optimum (minimum weight) shielding for specific applications can be designed only when the mission is fully defined.

From the above design goals, specific characteristics of the demonstration unit were evolved (Table 1). These characteristics were selected to make the demonstration unit as representative as possible of the ultimate power plants, to provide solutions to problems common to many applications, and to generally prove the feasibility of the concept.

Table 1 CHARACTERISTICS OF RISE DEMONSTRATION UNIT

Power level	3 kw(e)
Mission duration	10,000 hr (unattended)
Operating ambient temperature range	28 to 85°F
Maximum ambient seawater pressure	1000 psi
Resistance to	
Vibration	3 to 300 cps at 3 *g*
Shock	6 *g* triaxial
External radiation limits	
At 1 m from pressure hull	10 mr/hr
At pressure hull	200 mr/hr
Allowable misorientation	>±30°

Heat-Source Design Criterions

The proposed RISE heat source (Fig. 1) consists of 19 doubly encapsulated ^{60}Co fuel capsules embedded in the center of a spherical tungsten shield. Heat is transferred out by conduction through the shield to a helical coiled tube in which Dowtherm A is boiled. A spherical inner pressure vessel surrounds the coil and contains the NaK used as a heat-transfer medium between the shield and the coil containing the Dowtherm A. A vacuum space exists between the inner pressure vessel and the outer pressure vessel, which is designed to withstand the seawater pressure. The vacuum space limits heat loss during normal operation but can be filled with helium in an emergency to provide a heat path directly to the seawater. The outer pressure vessel is a hemisphere over the bottom half of the boiler joined to a cylinder to mate with the cylinder containing the power-conversion system. An aluminum adapter fills the space between the cylindrical portion of the outer pressure vessel and the upper hemisphere of the inner pressure vessel and provides a heat path from the upper boiler hemisphere to the seawater.

Screening of nine possible available isotope heat sources to select the radioisotope fuel for RISE, and particularly for the RISE demonstration unit, was done in two phases. In Phase I, selection criterions were established from the broad RISE mission and system plan and included operation in hydrospace for periods up to 10 thousand hr before refueling, and transfer of the heat from isotope decay to circulating Dowtherm A at approximately 700° F. The specific selection criterions were:

1. Minimum fuel half-life, 0.5 year: Consideration of a shorter half-life would complicate supply and restrict mission life.

2. All types of emitters are acceptable: Total cost of the fuel and shielding is the primary criterion for comparison of radioisotopes; the addition of shielding adds no premium cost so long as total weight and bulk is not excessive for the application or for the handling gear.

3. Melting point of the fuel form to exceed 1000° C: Molten fuels have not as yet been used. The limit chosen allows for the proper Dowtherm A operating temperature, normal temperature differentials in the fuel, cladding, shielding, and tubing, plus an allowance for minor temperature excursions.

These criterions and estimated costs were used as the basis for reducing the nine heat sources to three

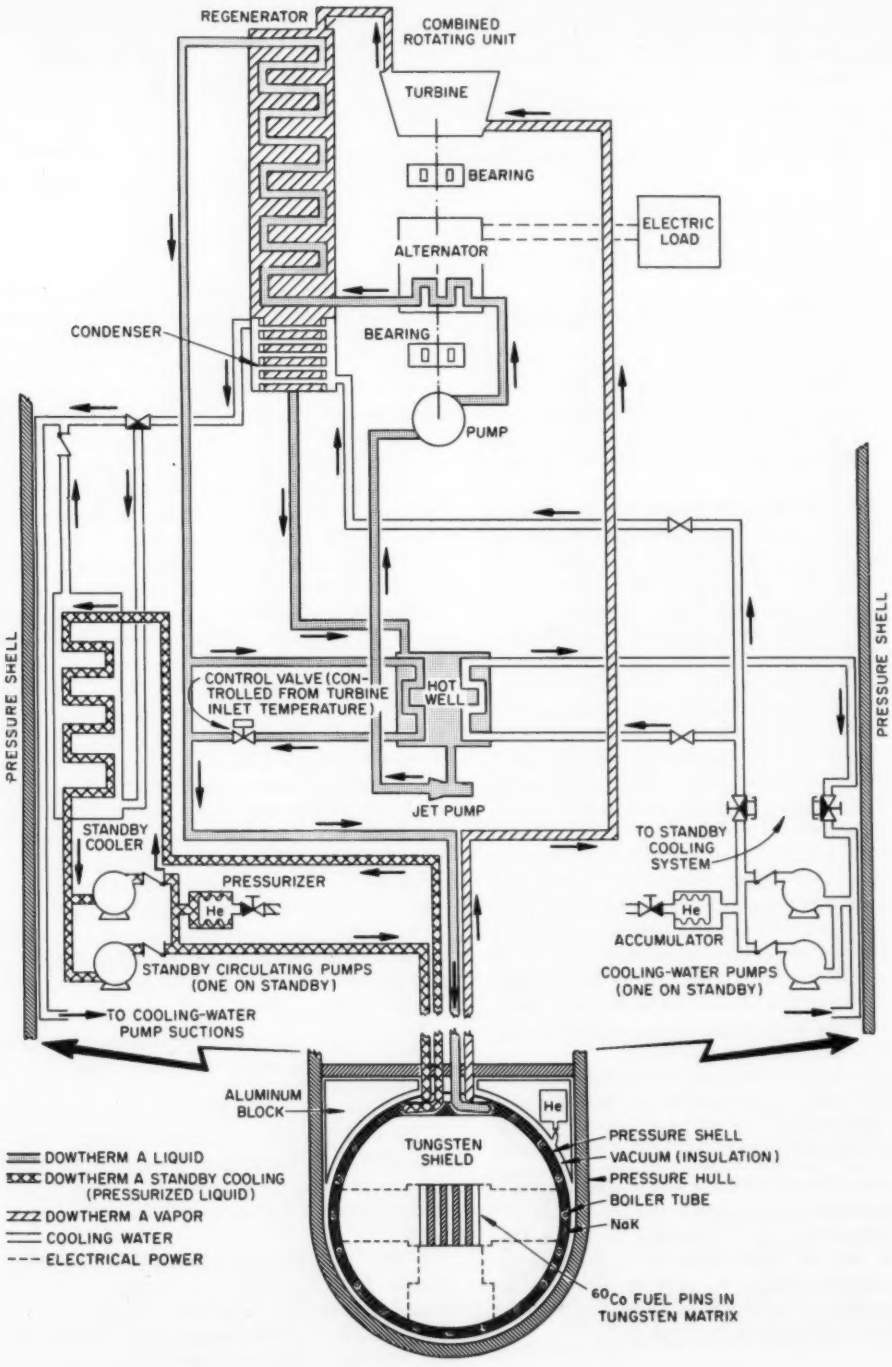


Fig. 1 RISE system schematic drawing. The boiler and power-conversion systems are to different scales.

candidate fuel forms: ^{60}Co metal, ^{90}Sr titanate, and ^{144}Ce oxide: The evaluation is summarized in Table 2.

The major considerations in Phase II of the fuel selection were availability and applicability for the RISE demonstration. It was assumed that the RISE demonstration boiler would be fueled within 2 years after start of program, and the engine would deliver 3 kw(e) continuously for 10 thousand hr, at an end-of-mission overall efficiency of 14.9%. Fuel activity would then be:

Table 2 PHASE I FUEL SELECTION

Isotope	Half-life, years	Fuel costs,* $/thermal watt	Fuel form	Melting point, °C
^{60}Co	5.24	18–33	Metal	1495
^{90}Sr	28	19–25	Titanate	1970
^{137}Cs	30	21–26	Several	<1000†
^{144}Ce	0.78	1.00	Oxide	1692
^{147}Pm	2.62	90–335†	-	-
^{210}Po	0.38†	-	-	-
^{238}Pu	89	>1000†	-	-
^{242}Cm	0.45†	-	-	-
^{244}Cm	18	>400†	-	-

*Cost data are based on recent estimates (private communication) by Savannah River Laboratory, Isochem, Inc., and Battelle–Northwest. Costs for ^{60}Co are current, but all others are projected, based on large-scale processing. In considering current costs only, ^{60}Co is apparently the only fuel available at less than $100 per thermal watt generated.

†Characteristic that caused rejection of the radioisotope for use in RISE.

Time	Megacuries		
	^{60}Co	^{90}Sr	^{144}Ce
Start of mission	1.59	3.45	7.20
End of mission	1.37	3.35	2.62

The availability of cerium and strontium from development laboratories was discussed with fuel development contractors who were doubtful that sufficient source material with relatively high ^{144}Ce or ^{90}Sr content would be available within the demonstration schedule. The moderately short half-life of ^{144}Ce and low power density of ^{90}Sr present added complications to the use of these isotopes. For these reasons, ^{90}Sr and ^{144}Ce were eliminated. On the other hand, ^{60}Co is ideally suited for the demonstration for several reasons and is the leading fuel candidate for RISE missions.

The Savannah River Plant has demonstrated production of ^{60}Co in metal form to a level of more than 200 curies/g. The process is as follows: The natural cobalt metal, ^{59}Co, is formed, plated with nickel, and loaded into irradiation capsules with aluminum spacers separating the cobalt to maintain a satisfactory blackness in the irradiation geometry. The irradiated cobalt metal is used directly as a heat source without further chemical processing; however, the reactor requirement for limited cobalt density is in direct opposition to the high power density desired in a heat source. The cobalt thus must be reencapsulated into fuel pins after irradiation, but the operations are restricted to packaging and capsule sealing. Fuel conversion or forming is unnecessary, and less stringent specialization in hot-cell equipment and technique is required.

An evaluation of the possible fuels indicates that ^{60}Co is also the leading candidate for later RISE missions as well as for the demonstration unit. Its high thermal conductivity as a metal is an inherent attraction in heat-source applications. The metal has a power density of 27 watts/cm^3 (at 200 curies/g) which compares well with ^{144}Ce oxide at 24 watts/cm^3 and far surpasses ^{90}Sr titanate at 0.9 watt/cm^3. The half-life of ^{60}Co (5.24 years) is well suited to the expected RISE missions, and the existing reactor capacity could produce enough fuel for many RISE engines.

FUEL SPECIFICATION

Each pin of the cobalt fuel will be doubly encapsulated in a tantalum liner and a Hastelloy C capsule. Helium-filled gaps are provided at the top of both containers to facilitate leak checking. The fuel charge will be distributed among 19 pins or capsules, each pin containing 143 cobalt disks, and the pins will be placed in holes arranged in a tungsten matrix at the center of the tungsten shield. Fueling will be accomplished by handling each pin separately to minimize requirements for heat dissipation. The axial clearance between the capsule and hole provides for differential thermal expansion of the fuel and shield (the thermal coefficient for Hastelloy C is approximately three times that of tungsten). The cladding and liner are shrink-fitted at room temperature, and the capsule and hole diameters are equal at nominal operating temperature. These close fits will minimize resistance to thermal conduction between the fuel and tungsten. The tungsten holes may be coated with inert material for a barrier between the tungsten and Hastelloy C fuel cladding to prevent self-welding.

SHIELD DESIGN

The 1.17- and 1.33-Mev gamma rays emitted by ^{60}Co must be shielded to prevent radiolysis of the Dowtherm A working fluid and to meet radiation-protection criterions. Approximately 3 in. of tungsten would reduce the gamma dose rate to a level where radiolysis of Dowtherm A will be insignificant over a 10-thousand-hr operating period, but approximately 7 in. is required for biological safety. The Dowtherm A tubing could, therefore, be located in a split shield; however, this configuration would increase both shield weight and fabrication problems. Hence it was decided to locate the Dowtherm A boiling coil outside the biological shield.

Although tungsten is a less efficient gamma-ray shield than uranium per unit weight, tungsten was

chosen because of its superior thermal conductivity (roughly three times that of uranium). The temperature difference between the boiler core and the Dowtherm A coil is therefore roughly one-third as great with tungsten as with uranium.

Large gamma-ray sources absorb a high percentage of the gamma-ray energy produced in the source. This effect is enhanced in the RISE heat source because of the relatively large volume fraction of tungsten in the fuel region. Calculations indicate that 74% of the total power is generated in the fuel region, while 26% is generated in the shield, primarily in the 2 in. nearest the fuel. Roughly 5% of the thermal power is due to the low energy beta radiation which is entirely absorbed within the core.

The size of the tungsten biological shield was chosen to meet the conservative criterions (radiation dose rate limited to a maximum of 200 mrem/hr at the boiler surface and 10 mrem/hr at 1 m from the surface) established by the Interstate Commerce Commission (ICC) for unattended shipments of radiation sources by common carriers. The RISE system can be handled without auxiliary shielding; however, as a result of the conservative approach taken, the shield thickness and weight may be greater than necessary for a specific mission. When mission requirements are better defined, the shield thickness and weight can probably be reduced. In addition, changes pending in the ICC transport regulations relax the radiation-dose-rate criterions for a controlled shipment of a single radiation source, as would be the case with RISE. These changes have not been factored into the design since they are not yet in effect.

HEAT TRANSFER

The heat generated by the cobalt fuel is transferred to Dowtherm A in the boiler tube by several modes: conduction and radiation through the helium cover gas between the cobalt disks and the fuel-pin wall; conduction through the tungsten shield; and forced convection and boiling in the boiler tube. The region between the shield and inner pressure vessel in which the boiler tube is located is filled with NaK to provide a good conduction path between the shield and the boiler tube wall.

The exterior of the inner pressure vessel is vacuum insulated to reduce heat losses during normal operation; however, the entire isotopic heat load must be transferred across this insulation to the sea in the event of an emergency when Dowtherm A no longer circulates in either the boiler or standby heat-removal tubes. To satisfy the requirement for an insulation which normally insulates but is a good conductor during emergencies, a single barrier located in the 0.1-in. gap between the inner and outer pressure vessels has been provided. This gap is evacuated during normal operation, thereby eliminating conduction heat losses across the gap. In the event of an emergency, the gap is flooded with helium, and the entire heat load is conducted through the helium to the sea.

In the boiler tube, 336 lb/hr of Dowtherm A is preheated to the saturation temperature (697° F), is vaporized, and then is superheated 3° F. This is accomplished in a 78-ft-long, 0.625-in.-OD, 0.575-in.-ID Hastelloy C tube that is wound around the exterior of the shield. There are three modes of heat transfer in the tube: forced convection to a liquid in the preheating region; two-phase boiling in the low-quality vaporizing region; and forced convection to a vapor in the superheating and high-quality vaporizing regions.

Power-Conversion-System Design Criterions

The purpose of the power-conversion system is to convert the thermal energy produced by nuclear decay of the isotopic fuel into usable electric power. The design of the system is affected by many factors, of which cycle efficiency, system weight, and system volume are usually the most significant. For mobile or semiportable power systems, overall size and weight are the most critical factors; however, for applications in hydrospace (deep submergence), radioisotope-fueled power systems are somewhat less sensitive to size and weight, and more sensitive to overall cycle efficiency and long-term reliability.

Long-term operating reliability is of major concern since the remote location of the system imposes limited accessibility for maintenance and servicing; overall efficiency is also of major concern since it directly influences the required isotope inventory and the associated fuel costs. The organic Rankine cycle provides high operating efficiencies with small weight and volume, combined with the capability for long life.

The power-conversion system incorporates a closed Rankine thermodynamic cycle with the turbine directly coupled to the alternator and liquid pump (Fig. 1). The cycle processes are consistent with those of conventional Rankine cycles. The liquid working fluid, Dowtherm A, is pumped to maximum cycle pressure, heated to saturated conditions, boiled, superheated slightly, and then expanded through the turbine. The low-pressure turbine exhaust vapor is cooled to saturated vapor conditions, condensed, and subcooled slightly, whereupon it reenters the pump to repeat the cycle.

COMBINED ROTATING UNIT

The heart of the power-conversion system is the combined rotating unit, which consists of a turbine, alternator, and pump mounted on a single shaft. The shaft is supported by two sets of radial hydrodynamic tilting-pad bearings and a set of counterposed hydrodynamic tilting-pad thrust bearings. The general design approach used for this machine provides the

developmental versatility and, simultaneously, the long-term operational integrity required for systems testing.

Turbine. Based on the performance-optimization study, the following characteristics were defined for the partial-admission, impulse turbine:

Turbine speed: 24,000 rpm
Turbine inlet pressure: 104.4 psia
Turbine inlet temperature: 700° F
Turbine exhaust pressure: 0.75 psia
Wheel pitch diameter: 7.25 in.
Number of turbine blades: 115

Alternator. The alternator is a homopolar inductor type, rated at 3.25 kw(e), directly coupled to and driven by the turbine at 24,000 rpm. The alternator operates in Dowtherm A vapor at a pressure of 0.5 psia. Liquid Dowtherm A passes through a spiral passage in the alternator housing to cool the unit. The alternator is designed to operate for more than 10 thousand hr without maintenance.

Selection of the homopolar inductor alternator is based upon its inherently rugged and reliable rotor construction which does not require the use of composite construction techniques. Because of the magnetic circuit arrangement in the homopolar inductor machine, rotating windings, bars, cages, or magnets are not required in the rotor of the machine. Brushes, slip rings, or other means of supplying electrical power to the rotor are also eliminated. The excitation winding of the machine is located in the stator and is incorporated into the stator insulation system.

The alternator design and fabrication techniques were chosen to provide a machine of highest possible performance and reliability. High-temperature hermetic connectors are used to bring the alternator winding connections through the stator housing. The alternator is designed to provide 1600 cps, 120/208 volts a-c, three-phase output.

Pump. A detailed pump study was completed to select the best type of pump. The specific speed for this application falls in a range where either a Pitot or partial-emission centrifugal pump could be used with approximately the same theoretical efficiency. Analytical relationships were established to define the actual expected pump efficiency and the resulting values compared to test data.

Although the partial-emission centrifugal pump provides higher efficiency, it also requires greater net positive suction heads or lower operating suction specific speeds than the Pitot pump. By using a jet pump inducer, the partial-emission pump can operate satisfactorily. Even though the overall pumping efficiency of the centrifugal-jet pump combination is penalized by jet pump primary pumping power, this combination still provides better overall performance than the Pitot pump.

REGENERATOR

The regenerator consists of a bundle of stainless-steel finned tubes, surrounded by a stainless-steel shell. Vapor from the turbine exit flows across the tubes in a single pass through the shell. Liquid Dowtherm A flows through the tubes in a three-tube parallel flow arrangement.

The design of the regenerator was influenced primarily by the low pressure of the vapor leaving the turbine. A low pressure limits the allowable pressure drop through the regenerator and controls the frontal area. Packaging and envelope restrictions resulted in a maximum allowable frontal area of 60 sq in. in the form of a rectangular duct, with sides of 5 and 12 in. Although a larger frontal area could be realized by using a nonrectangular cross section, it was not considered necessary with the defined envelope length.

CONDENSER AND HEAT-REJECTION SYSTEM

The Dowtherm A condenser consists of eight rows of ¼-in. plain tubes located in the lower end of the regenerator shell parallel to the regenerator finned tubes. Slightly superheated Dowtherm A vapor leaving the regenerator condenses as it flows across the condenser tubes. The saturated liquid condensate drains by gravity to the hot well. The heat of condensation is transferred to water pumped in a single pass through the condenser tubes and then through tubes located on the cylindrical pressure shell, where the waste heat is transferred from the cooling water through the pressure shell wall to the surrounding seawater.

There are several reasons for selecting an intermediate-loop heat-rejection system. This loop eliminates the possibility of freezing of Dowtherm A in a direct Dowtherm A-to-seawater condenser at seawater temperatures below 53° F. The dual loop concept is desirable due to the high condensing temperature (290° F) and the need to keep metal surfaces in contact with seawater below about 150° F to prevent scaling. Control of the hot-well temperature is most easily accomplished in a dual loop system.

A surface area of 23 sq ft on the straight section of the power-conversion-system pressure shell is used for the natural convection heat rejection. Pressurized water in the intermediate loop is pumped through forty ¼-in.-OD tubes brazed to the inside of the pressure shell.

The pressure hull section is sized for heat rejection to a maximum seawater temperature of 85° F during the several modes of RISE operation. The intermediate water loop heat load during normal operation is the sum of the condenser heat-rejection load and the excess isotope power. During standby operation while RISE is submerged, the water loop rejects the total radioisotope power. The intermediate loop water flow rate is 8.7 gal/min initially. During normal operation this pump capacity is divided between the condenser flow of 7.3 gal/min and the hot-well heat-

exchanger flow which decreases over the system life from an initial value of 1.4 gal/min. During standby cooling the total pump output is directed to the standby cooling heat exchanger.

The water loop is pressurized to 150 psia to prevent boiling of the water in the standby cooling heat exchanger. Water loop pressure is maintained by cover gas pressure in a small water loop pressurizer.

EXCESS-ENERGY-REJECTION SYSTEM

The function of the excess-energy-rejection system is to transfer the isotope thermal energy that is in excess of the power-conversion-system needs to the cooling water. This energy excess results from the difference between the power-conversion heat-energy needs, which are constant, and the isotope energy production rate, which decays approximately 15% during 10 thousand hr. The excess-heat-rejection process could be handled by a separate coolant loop at the boiler; however, the control of such a loop to maintain a constant energy input to the power system would pose a major control problem. To eliminate this problem, the system was designed to reject excess heat through the working fluid. This is done by cooling a portion of the Dowtherm A before it enters the boiler; consequently, the excess isotope energy is required to heat the liquid prior to boiling. The trim heat rejection system is shown schematically in Fig. 1. A portion of the liquid Dowtherm A is diverted at the exit of the regenerator into a heat exchanger which recools the liquid by rejecting the heat to the water cooling system. The amount of fluid diverted is regulated by an automatic valve controlled by the turbine inlet temperature. As turbine inlet temperature tends to drop with decreasing isotope heat rate, the valve closes, diverting less liquid to the heat exchanger, and thus maintains an essentially constant turbine inlet temperature. An orifice is included in the main line from the regenerator to the boiler to balance the pressure drop through the trim heat exchanger and control valve. The maximum flow which must be diverted to reject the initial excess energy is approximately 20% of the turbine flow rate.

INSTRUMENTATION AND CONTROL SYSTEMS

The details of the instrumentation and control systems as well as methods for startup and standby operation are given in Ref. 3.

(Robert H. Lafferty, Jr.)

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COMPACT AND VERSATILE RADIOISOTOPE HEATERS

Atomics International, a Division of North American Aviation, Inc., 8900 Desoto Avenue, Canoga Park, Calif., is producing and selling commercial models of a compact, e.g., a 5-watt(t) unit weighing 2 lb, radioisotope heat source, i.e., a source in which the kinetic energy of the electromagnetic or charged-particle products of radioisotope decay is converted to heat rather than to electricity. A ThermoPac heater fueled with one of several radioisotopes—^{60}Co, ^{137}Cs, ^{147}Pm, ^{170}Tm, ^{210}Po, or ^{238}Pu—is available to meet the varying demands for lifetime, weight, shielding, or cost that depend upon the intended application, such as instrument temperature control, catalyst heating, or spacecraft temperature control, and the specific location—aerospace, marine, or terrestrial.

ThermoPac heater units are available to provide reliable thermal power [0.1 to 100 watts(t)] in configurations tailored to specific needs. Total costs of units vary with unit design requirements.

(Joan E. Carden)

Section VI

Isotopes and Radiation Technology

Isotopes Around the World

Manufacture of Radioisotopes, Sources, and Labeled Compounds in Czechoslovakia*

By Karol Chorvát†

Czechoslovakia's requirements for radioactive materials are met by import and by manufacture. Some 600 radioisotope consignments are now received from abroad annually, and 6000 to 8000 shipments are made to customers, both domestic and foreign.

Radioactive materials are produced at two laboratories in Czechoslovakia. The Ústav pro výzkum, výrobu a využití radioizotopů (Radioisotope Research, Production, and Utilization Institute), in Prague, distributes and monitors both imported and manufactured radioisotopes throughout the country; produces labeled organic compounds, sealed sources, neutron sources, radioactive luminous pigments, and standards; conducts research and investigates applications of radioisotopes in industry; disposes of radioactive waste; and provides a central service for individual film dosimetry. The Ústav jaderného výzkumu ČSAV (Czechoslovak Academy of Sciences Nuclear Research Institute) at Řež, the nuclear research center, has the VVR-S research reactor, with a maximum thermal power of 4 Mw, and the U-120 cyclotron, with maximum energies of 12.5 Mev for deuterons and 25 Mev for alpha particles.

The average annual value of the radioactive materials supplied to laboratories in Czechoslovakia in 1961 to 1963 was $410 thousand (6.56 million Kčs) (imported plus manufactured), which is $283 thousand per 10 million inhabitants. (The average value for 3 years is taken because of a large issue of high-activity sources in 1962.) The figure does not include costs of distribution and monitoring, which would add another 15%. The average per capita value for this period was about the same as that of the United Kingdom and Belgium in 1962, and about 60% that of the United States. In 1965, laboratories in Czechoslovakia were supplied with $505 thousand worth of radioisotopes, sources, and labeled compounds, which is $358 thousand per 10 million inhabitants. This is a 19% increase over the 1961 to 1963 average. One-fourth of the radioactive materials consumed was manufactured in Czechoslovakia.

Use

The number of installations acquiring radioactive materials has increased from 40 in 1955 to 240 in 1965:

Year	No. of users	Year	No. of users
1955	40	1961	192
1956	51	1962	193
1957	68	1963	205
1958	150	1964	221
1959	143	1965	240
1960	176		

These numbers do not include all laboratories using low-activity sealed sources containing ^{60}Co, ^{137}Cs, or ^{90}Sr. The 240 consumers in 1965 were distributed as follows: research 35%, medicine 26%, industry 18%, teaching 18%, others 3%. In comparison with other countries, the extension of radioisotope applications to other laboratories is not entirely satisfactory, and more attention should be given to technical publicity and expansion of radioisotope methods. The greatest possibilities appear to be in wider use of measuring techniques in industries and the development of diagnostic and therapeutic methods in medicine.

About 90 different nuclides are now being used. There is a relatively high and constant demand for

*Abbreviated and edited version of article, in Czech, in *Jaderna Energie*, 12: 225-227(1966) (translated into English by J. B. Sykes, AERE-Trans-1068).

†Institute for Radioisotope Research, Production, and Utilization, Prague.

Table 1 DEVELOPMENT OF RADIOISOTOPE DEMAND IN CZECHOSLOVAKIA

Isotope	Amount, curies								
	1957	1958	1959	1960	1961	1962	1963	1964	1965
^{3}H	-	16	1,789	2,254	521	662	495	95	331
^{14}C	0.5	1	1	2	2	2	2	1	8.5
^{24}Na	0.5	1	1	3	3	4	8	5	3.5
^{32}P	7.5	17	15	21	19	13	11	12	12
^{35}S	1.5	5	7	8	5	4	3	3	3
^{60}Co	7.5	1,359	87	10,658	4,390	26,975	12,346	8,150	29,787
^{90}Sr	6	4	2	5	3	7	6	4	2
^{131}I	17	22	21	28	24	25	25	28	32
^{137}Cs	3.5	43	6	41	345	2,893	392	88	980
^{192}Ir	12	61	71	63	52	90	149	270	623
^{198}Au	4.5	26	46	37	29	28	27	28	34
Other	4.5	13	12	87	103	70	203	349	231
Total	65	1,568	2,058	13,207	5,496	30,773	13,667	9,033	32,047

^{60}Co, ^{131}I, and ^{198}Au (Table 1). The demand is increasing for ^{192}Ir and for other isotopes as a whole, although that for ^{32}P and ^{35}S is falling. Demands for tritium and for ^{137}Cs vary.

Sealed ^{60}Co sources, which each year account for more than 90% of the total activity of radioisotopes distributed, are used mainly for large gamma-radiation sources (e.g., at ÚJV ČSAV, ÚVVVR, and other laboratories); large quantities of ^{60}Co are used in teletherapy radiation units for medical work.

Production

The research reactor at ÚJV ČSAV has been used mainly to produce the short-lived isotopes ^{24}Na, ^{42}K, ^{64}Cu, ^{76}As, ^{82}Br, ^{110}Ag, ^{124}Sb, ^{203}Hg, ^{32}P, ^{35}S, and simple forms of some others—^{51}Cr, ^{72}Ga, ^{75}Se, ^{86}Rb, ^{90}Y, ^{99}Mo, and ^{115}Cd. The VVR-S reactor is used chiefly for research, and the range and quantity of radioisotopes produced are small in comparison with those in similar reactors in other countries. To meet the demand of laboratories in Czechoslovakia for radioisotopes of short and medium half-life—especially ^{131}I, ^{198}Au, ^{90}Y, and ^{51}Cr in the form of radiopharmaceuticals—it will be necessary to extend the range of radioisotopes obtained by reactor irradiation of targets. This will be possible after completion of the trial operation of a new suite of hot laboratories at ÚJV ČSAV.

The ÚJV ČSAV cyclotron is used to prepare carrier-free ^{48}V, ^{52}Mn, and ^{85}Sr, and some others are to be made available—^{54}Mn, ^{57}Co, and sterilized ^{85}Sr solution for medical use. We may expect increasing use of cyclotron-produced radioisotopes, and it is therefore desirable to consider, eventually, the production of other radioisotopes.

The main emphasis on radioactive materials production in Czechoslovakia, in both extent and value, is in the ÚVVVR production program. Organic compounds labeled with ^{14}C, ^{3}H, and ^{35}S are prepared in wide variety, mainly for biochemical and medical research. All compounds have a high degree of radiochemical purity.

Most of the compounds labeled with ^{14}C are prepared by biosynthesis, using the alga *Chlorella* grown in a $^{14}CO_2$ medium. By various methods of isolation and compound utilization, ^{14}C-labeled amino acids, sugars, ribonucleosides, deoxyribonucleosides, ribonucleotides, and purine and pyrimidine bases have been made with high specific activity. Some of the ^{14}C-labeled compounds prepared by synthesis and biosynthesis are thymine-2-^{14}C, thymidine-2-^{14}C, thymine-(methyl-^{14}C), thymidine-(methyl-^{14}C), and 6-azauracilriboside-4,5-^{14}C.

The compounds thymine-6-^{3}H, thymidine-6-^{3}H, thymine-(methyl-^{3}H), thymidine-(methyl-^{3}H), uracil-5-^{3}H, and others of specific activity 1 to 10 curies/millimole are prepared with gaseous tritium.

Isotope exchange is used to prepare ^{35}S-labeled compounds with specific activities of 10 to 50 mc/millimole.

Sterile solutions of Hippuran and Rose-Bengal labeled with ^{131}I are made for kidney- and liver-disease diagnosis.

For treatment of malignant tumors, ^{226}Ra sources are made in the form of needles or double-walled tubes. The half-life of ^{226}Ra, 1620 years, makes possible a constant source activity.

Flat sources, in the form of strips and disks, of ^{90}Sr, ^{147}Pm, ^{204}Tl, ^{239}Pu, etc., are made by powder-metallurgy methods. They are used in radioisotope gages for measurement of thickness, density, and levels; to eliminate electrostatic charges; and in fire alarms.

Luminous pigments containing ^{226}Ra and ^{147}Pm are also made in various activities and colors, as well as ^{226}Ra gamma sources and Ra–Be neutron sources of up to 1000 mg of radium. Production of luminous pigments containing tritium will begin shortly.

This Institute also produces a series of standards, containing various radioisotopes, for calibrating radiation detectors, dosimetric apparatus, and gamma-scintillation spectrometers and for use as reference sources in relative activity measure-

ments. Very good results have been obtained with standards in international comparison measurements.

A large part of the radioactive materials produced is exported. In 1964 the value of exports was 45% of the total value manufactured. Export of labeled compounds, radioactive luminous pigments, sealed sources, and other products showed a rise in 1965, with 55% being sent abroad. The majority of the exports are labeled compounds for biochemical and medical research.

A continued expansion of international collaboration and trade between Czechoslovakia and other countries in meeting the requirements of user laboratories may be expected in the future. We can expect a further increase in the demand for radioactive materials, both quantitative and qualitative, and extended uses of radioisotopes. In the production of radioactive materials, there will be increased demands on radiochemical and chemical purity of the products, specific activity, and choice of radioisotopes whose physical and nuclear properties allow the best solution to specific problems. The radioactive materials manufacturing and distributing organizations must meet Czechoslovakia's demand for high-quality radioisotopes, sealed sources, and labeled compounds; develop the country's production; and make the maximum use of existing and planned nuclear apparatus. (MG)

Ten Years of IAEA Isotope Work*

On 29 July 1957, the International Atomic Energy Agency (IAEA) came legally into being with 26 countries as members. Eighteen ratifications were required with at least three from among the five leading atom powers (Canada, France, USSR, UK, and USA). Today, 98 countries are members. The creation of the IAEA was the first successful step toward the setting up of international machinery for controlling the hazards and promoting the beneficial potentialities inherent in nuclear energy.

One hundred and seventy-eight panels, 21 study groups, and 13 other meetings have been convened. The proceedings of the meetings, panel reports, surveys, manuals, scientific journals, etc., issued by the Agency, largely in English, French, Russian, and Spanish, total nearly a thousand titles, making the IAEA one of the largest publishing houses in the atomic field.

Among the areas in which the IAEA has worked, an obvious field for attention has been the ways in which isotopes can be applied—easily, often cheaply, and with a promise of relatively quick practical results, particularly in developing countries. The main activities have been:

In Agriculture: Improvement of yields through better use of fertilizers, mainly for rice studied in 12 countries and for maize in 8 countries; production of better rice, wheat, and barley through radiation-induced mutations; control or eradication of insect pests, e.g., the fruit fly in Central America and the olive fly in Greece; protection of food against contamination; work on the preservation of stored food by irradiation; studies designed to make optimal use of water in the soil; and preparation by irradiation of vaccine for animals against long worm.

In Hydrology: Since 1960 the Agency has been carrying out, jointly with the World Meteorological Organization (WMO), a continuing world survey of the content of tritium and certain stable isotopes in precipitation to determine the water turnover on earth; 22 countries were helped with studies on their local water development problems, mainly to ensure the best possible use of underground or surface water resources; studies on 20 major rivers in various parts of the world were carried out jointly with UNESCO within the International Hydrology Decade program.

In Medicine: Goiter research ranged from the heights of the Andes in Peru to those of the Himalayas in Nepal; arrangements for the provision of equipment for radiological treatment of cancer were made for 7 countries; research on goiter, anemia, malnutrition, and tropical diseases was promoted in 44 countries; radiosiotope techniques for medical diagnosis have been developed and standardized.

In Industry: The IAEA has endeavored to acquaint countries with radioisotope techniques for improving the quality or the production of manufactured goods; for process, wear and tear, and flow control; and for sterilization of medical products—all ways to realize savings of the order of hundreds of millions of dollars per year.

Much of this research has been done at the Agency's own laboratories, unique in their international character, but the Agency has also been able to direct internationally concerted efforts at the solution of specific scientific problems. A provisional laboratory, set up in 1958 to study physics and low-activity chemistry, has been maintained for

*Shortened form of IAEA Press Release PR 67/45, 25 July 1967.

hydrological work and for investigations on radiation accidentally or medically introduced into the human body. An Agency-developed whole-body counter is used in this work. A functional laboratory at Seibersdorf, some 20 miles southeast of Vienna, has been in operation since 1961, with sections for physics, chemistry, hydrology, and medical physics. It has dealt with questions as different as the fallout content in foodstuffs, meteorites, ores, and sedimentation in rivers. Radioisotope standards prepared by the Agency—7358 samples have been ordered since 1963—and dispatched throughout the world have served to calibrate instruments and check on research work in 56 countries.

The Middle Eastern Regional Radioisotope Centre for the Arab countries was set up under the auspices of the IAEA in Cairo, UAR, in 1963 for the training of specialists in radioisotope techniques and for research.

Most of the Agency-sponsored research has been done under 550 research contracts or agreements, awarded to institutes in 61 countries, at a total cost of $6.5 million. The main subjects have been radioisotope applications in agriculture, hydrology, medicine, biology, and industry; food preservation by irradiation; reactor studies; radioactive waste disposal; radiation protection; and development of safeguards procedures.

As a corollary to the rapidly growing use of radioactive materials both for isotope work and power production, the IAEA's protective functions have assumed increasing importance. The Basic Safety Standards for Radiation Protection and the Regulations for the Safe Transport of Radioactive Materials evolved by the Agency, and mandatory for all activities with which it is connected, have already served as the basis for national radiation-protection legislation in many countries. More than 97,000 copies of the IAEA's manuals for safe handling of radioactive materials have been distributed throughout the world.

Much of what the Agency has been able to achieve during the first decade of its existence is due to the close links and the cooperation established with other international organizations, both governmental and nongovernmental. The IAEA, which is an autonomous body, has concluded agreements with the United Nations (UN) and with seven of its specialized agencies. With one of them, the Food and Agriculture Organization (FAO), a Joint Division of Atomic Energy in Food and Agriculture has even been set up at the Agency's Headquarters in Vienna. Particularly close links have been established with the World Health Organization (WHO) and with the European Nuclear Energy Agency of the Organization for Economic Cooperation and Development (ENEA). The Agency has been participating in various projects financed from the UN Special Fund and Expanded Programme of Technical Assistance (EPTA) and has acted as executing agency for a number of major UN Development Programme (UNDP) projects.

The IAEA staff at Headquarters and its various laboratories, centers, etc., coming from 53 different nationalities, includes about 300 scientists and other professionals. (Martha Gerrard)

Production and Sales of Radioelements in France*

In 1966, of 55,800 shipments of radioisotopes made by the French Commissariat à l'Energie Atomique (CEA), 7458 were to fill export orders. Total sales were $1.76 million, of which 42% were from export. The $300 thousand worth of radioelements produced for the CEA itself brings the total value of radioelements produced to $2.06 million. Total sales in 1965 were $1.33 million, 36% of which were for export. The 1966 values are the highest of any year since the CEA started the production of radionuclides in the Zoé reactor at Chatillon in 1949. In that year there were 126 shipments of radionuclides. Shipments have continued to increase in subsequent years; for example:

1954	2,119
1959	7,247 ($180 thousand)
1964	41,778 ($1.09 million)

There were no exports prior to 1957.

The major quantities of radionuclides produced and delivered in 1966 were

70,700 curies of low-specific-activity radionuclides
^{60}Co for teletherapy
33,000 curies of ^{137}Cs
19,196 curies of ^{192}Ir
454 curies of ^{131}I
284 curies of colloidal ^{198}Au
116 curies of ^{32}P

*Based on "Production and Sales of Radioelements," in *Bull. d'Information Scientifique et Technique (Paris)*, No. 114, p. V, April 1965, and "20 Years of Studying Materials," by H. Pratier, especially "The Radioelements," *Energie Nucléaire*, 7: 494-497 (1965) (English translation in USAEC file No. NP-tr-1392). A review of this subject a year ago included production data through 1965 and a detailed discussion of uses [*Isotopes and Radiation Technology*, 4(2): 189-194, by C. Fisher, "Production and Use of Radioisotopes in France"].

The 2062 French uses of radionuclides in 1966—10.5% more than in 1965—were broken down as 1235 industrial, 663 research, and 164 medical.

Radionuclides have been made in France in both the CEA research reactors and the Marcoule power reactors. Commissioning of the Osiris pool reactor will increase considerably the production capacity for radionuclides, and, from 1967 on, ^{60}Co will be produced by Electricité de France's nuclear power stations. The ^{60}Co used for teletherapy is produced by the Belgian BR-2 reactor within the framework of the association among CEA, the Belgian Nuclear Energy Research Center, and the Italian company SORIN.

Both ^{137}Cs and ^{90}Sr are isolated in the fission-product recovery program. A new ion-exchange facility has been constructed at Marcoule for recovering ^{137}Cs in thousand-curie—and later in hundred-thousand-curie—quantities. This facility can eventually be used to recover ^{90}Sr. A laboratory has been designed, to be built at The Hague, for producing very intense ^{137}Cs and ^{90}Sr sources.

CEA has awarded a number of design or development contracts to industry, including those for study of optimization of industrial sources, applications of tracers, activation analysis, and X-ray fluorescence. Hydrology, sedimentology, X-ray fluorescence, and the use of intense radiation have been studied by CEA at both the Grenoble and Saclay Nuclear Research centers. CEA also makes labeled compounds, which are of special interest in biological and medical research.

Since 1962, the manufacturing programs of CEA, the Belgian group, and the Italian group have been coordinated and their products listed in a common catalog, "Processed Isotopes and Sealed Sources."

CEA offers assistance to industrial and research groups interested in using radionuclides. A special service, jointly administered by Saclay and Grenoble, sends experts throughout France and abroad for consultation on uses of radioisotopes.

(Martha Gerrard)

BASIC SAFETY STANDARDS FOR RADIATION PROTECTION, 1967 Edition
Safety Series No. 9, IAEA, Vienna, 1967
vii + 79 pp., $2.00; distributed in the United States
by International Publications, Inc., New York

This edition of the IAEA Basic Safety Standards was approved by the Board of Governors in 1965 and changed slightly to incorporate ICRP 1966 recommendations. The standards apply both to workers and to the public individually and collectively, and they cover production, processing, handling, use, storage, transport, and disposal of radioactive material. Doses incurred from nuclear-test fallout, from medical diagnostic and therapeutic uses, and from natural radioactivity are excluded. Tables of maximum permissible organ concentrations and intakes of various radionuclides are appended. "Standards" is available in Russian, French, and Spanish as well as English. (MG)

SWEDISH ISOTOPE NEWS

The Swedish Isotope Techniques Laboratory keeps its customers and friends informed of current developments in isotope technology by means of a quarterly publication, *Isotopnytt* ("Isotope News"). Now in its seventh year, this useful circular prints abstracts, in Swedish, of pertinent articles from the world's literature, particularly from the less widely circulated journals and reports. Both news items and items on unusual applications are included. (MG)

Section VII

Isotopes and Radiation Technology

Miscellaneous

Conferences

Capri Experiment Results Reported to IAEA Panel

At a meeting of an international panel of experts on insect pest control in Vienna in August 1967, Dr. D. Nadel reported that, although cold rainy spring weather interfered with the experiment, the attempt to use the sterile-male technique to rid the island of Capri of fruit flies has apparently been a success. The project was supported by the Italian government with assistance from the International Atomic Energy Agency (IAEA), the Food and Agriculture Organization of the United Nations (FAO), and the Israel Atomic Energy Agency. Traps and fruit samplings at key points on Capri have failed to detect any wild flies, which are suspected of coming from the mainland each year.

Other results reported concerned the use of the technique to eradicate a similar fruit fly from the Mariana Islands, including Guam, Rota, Saipan, and Tinian. IAEA is currently supporting or cooperating in research on the sterile-male technique in Austria, Belgium, the Federal Republic of Germany, Israel, Korea, Pakistan, and the United Arab Republic. Countries involved in one experiment in Central America include Costa Rica, El Salvador, Guatemala, Honduras, Mexico, Nicaragua, and Panama.

IAEA Conference Compares Preservation of Fish by Freezing and by Irradiation*

An international conference on the freezing and irradiation of fish was held in Madrid on September 4–8, 1967. The conference was sponsored by the Food and Agriculture Organization of the United Nations, the International Institute of Refrigeration, and the International Atomic Energy Agency. About 250 scientists attended, representing 35 countries.

The conference was held in two parts; the first part dealt with the technology and economics of fish freezing, and the second part reviewed developments in fish irradiation. The papers presented on the status of the irradiation process varied from cautious optimism to outright assertions of demonstrated feasibility. The U. S., Italian, and Spanish representatives were enthusiastic; the English and Germans were concerned about the practicality of the process. Hobbs and Shewan (United Kingdom) presented an excellent objective analysis of the possible botulism hazard.

*The Isotopes Information Center has received copies of the papers on irradiation of fish; these will be summarized in an article in the Food Irradiation section of a later issue.

Availability of Isotopes and Services

ORNL Stable-Isotope Inventory Augmented

Recent additions to the ORNL enriched stable-isotope inventory include the following:

Isotope	Purity, %	Amount available, g
^{33}S	25.5	1.6
^{37}Cl	90.3	47.2
^{65}Cu	99.7	55.0
^{98}Mo	98.1	67.4
^{152}Gd	32.2	4.1
^{155}Gd	91.8	93.7
^{157}Gd	88.6	13.6
^{160}Gd	95.95	70.0
	99.99	8.6
^{196}Hg	55.8	0.9
	94.4	0.3
^{202}Hg	75.6	3.5
	76.8	4.3

ORNL Stable-Isotope Shipments Continue To Increase

Reflecting the expanding uses of separated stable isotopes in cross-section studies, in measurements of other nuclear and of extra-nuclear properties, and as targets for high-quality radioisotopes, the sales and loans of these enriched nuclides continue to increase. In 1966 there were nearly 3800 sales—an all-time high. Figure 1 shows the growth of the program since its inception in 1946. (PSB)

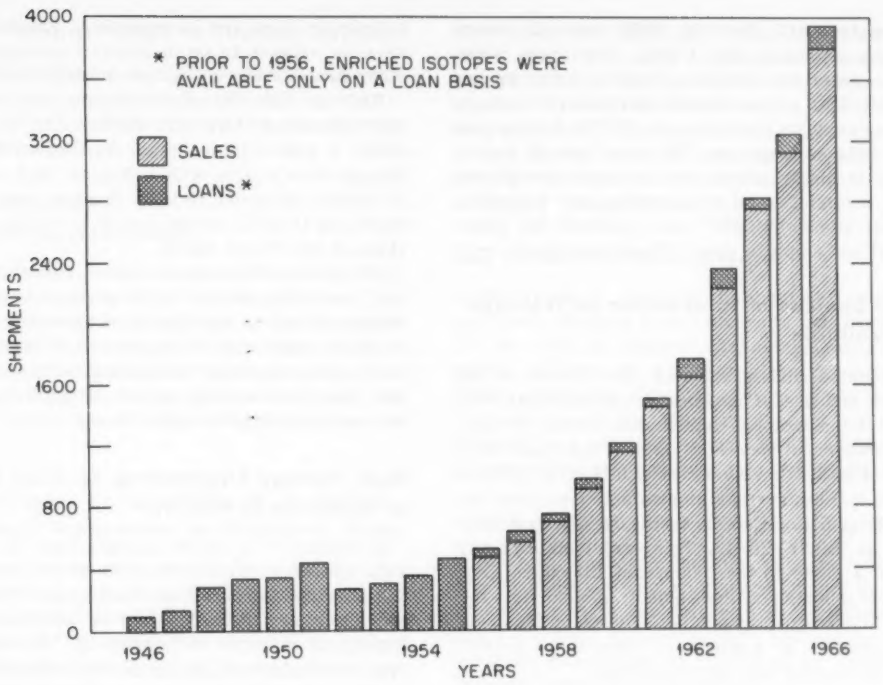

Fig. 1 Distribution of electromagnetically enriched stable isotopes, 1946–66.

Neutron Products Markets First Private ^{60}Co

The first sale of ^{60}Co produced in a private power reactor is 50 thousand curies from Neutron Products, Inc., to U. S. Nuclear Corp. The cobalt was produced as a by-product in Consumers Power Co.'s Big Rock Point reactor. The shipment was mixed solids (10 to 20 curies/g) and hollows (20 to 40 curies/g).

General Electric Supplies First Private Plutonium

General Electric Company has recovered about a gram of ^{238}Pu from a ^{237}Np target irradiated in the Vallecitos Test Reactor. General Electric is offering the plutonium at $25 per millicurie on orders of up to 100 mc and $10 per millicurie for larger orders. The relatively high prices are not meant to reflect the formal price structure to be established when GE goes into multigram production in 1968.

AEC Activities

Portable Cesium Food Irradiator Continues Demonstration Tour

The truck-mounted food irradiator using ^{137}Cs as the radiation source is continuing its cross-country tour, visiting private firms and demonstrating the benefits and commercial potential of food preservation by irradiation. The tour began at Arlington, Mass., in August 1967 and has continued through Pennsylvania, Ohio, and Nebraska; 12 companies have used the irradiator so far. The unit has now reached Washington State where it will operate for the next 6 months before moving southward along the Pacific Coast.

Foods irradiated during the national tour include tomatoes, onions, oranges, mushrooms, mink feed, and seeds. In Washington, wheat flour will be treated at Walla Walla and potatoes at Kennewick. The produce is furnished by growers and processors in the area and returned to them for observation and testing.

The irradiator uses a source of 170 thousand curies of ^{137}Cs installed at Brookhaven National Laboratory. Scheduling and programming of demonstration tests are directed by the Division of Isotopes Development of the USAEC. Isotopes, Inc., of Westwood, N. J., operates the unit, which was designed by Vitro Engineering Corp. of New York and built by American Nuclear Corp. of Oak Ridge.

NUMEC Boron Separation Contract Extended

The USAEC has announced that its contract with Nuclear Materials and Equipment Corp. (NUMEC) has

been extended until Dec. 31, 1969, with an option for further extension for 1 year. The costs of the contract—about $2 million annually—cover operation by NUMEC of the Commission's boron isotope separation plant at Lewiston, N. Y. The facility was built in 1954 to separate ^{10}B from natural boron. Boron-10 is highly useful as a neutron control and shielding material in nuclear reactors and in dosimetry applications. NUMEC has operated the plant since 1964 and employs about 115 persons there.

"Special Sources of Information on Isotopes" Now Available

An annotated bibliography of 830 entries on the production and use of isotopes has been prepared by the staff of the Isotopes Information Center. This is the 4th revision of *Special Sources of Information on Isotopes*. The 3rd revision was published in 1962 as TID-4563; the 4th revision is available free from the Isotopes Information Center, Oak Ridge National Laboratory, as ORNL-IIC-12. This useful bibliography serves as a guide to the permanent literature, i.e., books and reports, on the subject; it also lists the journals that frequently publish articles on isotopes. It is introduced by a summary view of the uses of isotopes in industry and research today.

Radioisotope Licensing Procedures for Medical Diagnosis Simplified

The proposed amendments to the procedure for licensing the use of radioisotopes in medical diagnosis have been made final by the USAEC. The proposal [see *Isotopes and Radiation Technology*, 4(2): 202 (Winter 1966–1967)] divides the most common diagnostic uses of radioisotopes into two groups and specifies that a license for the use of a radioisotope within a group is good for all uses in that group. Comments on the proposed amendment to Part 35 of the USAEC regulations led to the additional inclusion of four well-established diagnostic uses of radioisotopes. The amendments became effective 30 days after publication in the *Federal Register* on Oct. 14, 1967.

General

Radiation Dynamics Inc.—New Contract and New Financing

Radiation Dynamics Inc. (RDI), the developer of the Dynacote particle accelerator and curing process, has reached an agreement with Otto Dürr of Stuttgart to install a 300-kev Dynacote. The German firm, a manufacturer of industrial paint and curing equipment, will operate the facility and rent it to other European companies. Kennard Morganstern, President of RDI, says he expects to set up similar arrangements with other firms in Europe and the United States.

RDI has also recently completed an arrangement with Firestone Tire and Rubber Co. for financing under a joint-venture plan. Firestone is providing Morganstern's firm with a 3-year $1.5 million line of credit, repayable to 1976. For this, they may purchase, up to 1977, as much as 40% of RDI outstanding stock at $23.75 per share.

The joint-venture firm will do research in industrial radiation, attempting to develop marketable irradiated products and processes that would be licensed to other companies. Firestone would retain rights of first refusal on items concerning its current products. The giant tire company expects to put $1 million into the venture during the next 5 years.

High Voltage Engineering To Cure Coatings at Netherlands Facility

According to a recent announcement in its *Newsletter* (Vol. 2, No. 3, Summer 1967), High Voltage Engineering Corporation, Burlington, Mass., will provide a new radiation service and demonstration facility at its plant in Amersfoort, The Netherlands. The new facility will include a 500-kv insulated-core-transformer electron accelerator with conveyor for use in studying the curing of coatings on textiles, paper, and films. European industrial scientists and engineers should find this new service of great value.

Kaman Nuclear Develops Food-Analysis System

Kaman Nuclear has developed an analysis system, based on neutron activation analysis, to determine the protein content in grains. The neutron activation system consists of a fast neutron generator, a dual pneumatic transfer system for handling samples, radiation detectors, a sequence control device, and a scaler readout unit. An on-line analysis can be performed every 5 min with less than 1% error; this is a considerable improvement over the time-consuming conventional chemical analysis that is accurate to only 3%.

The system, which was developed with backing from the Corn Industries Research Foundation, was built and leased to Standard Brands' Clinton Corn Processing subsidiary for testing. Its successful operation will mean Kaman will sell the system for about $40 thousand to food product manufacturers.

Cobalt-60 Sale from AAEC to UKAEA

The Australian Atomic Energy Commission has reported the sale of a ^{60}Co source worth $35 thousand (Australian) to the United Kingdom Atomic Energy Authority's Radiochemical Centre.

Air Force Contract Goes to Thermo Electron

The Systems Engineering Group, Wright-Patterson Air Force Base, has awarded a $98,600 contract to the Thermo Electron Engineering Corp. for research on a ^{60}Co thermionic generator.

Air Force Contract for Sanders Nuclear Study

Sanders Nuclear Corp., a jointly owned subsidiary of Sanders Associates and Cambridge Nuclear, has received a contract for $100,000 from the Aerospace Medical Division, Brooks Air Force Base, to study the feasibility of an isotopically heated suit for emergency use by airmen. During the 4-month study, the firm will investigate a number of isotopes for use in the suit.

Gamma Process Co. and New York State's ASDA Reach Agreement on Radiation Plant

An agreement reached earlier between the New York State Atomic and Space Development Authority (ASDA) and Iso Nuclear Corp. has been confirmed by Gamma Process Co., which has subsequently bought out Iso Nuclear. The agreement concerns the construction and operation of a $1.5 million commercial radiation processing plant.

Under the terms of the agreement, ASDA will provide the site — about 5 acres located at the Western New York Nuclear Service Center near Buffalo — and $770 thousand. Gamma Process Co. will design, construct, and operate the plant. Gamma Process Co. will put up funds for the ^{60}Co source, special equipment, and operating costs. These funds will amount to $750 thousand, and Gamma Process Co. has applied to the Securities and Exchange Commission for permission to sell stock to the public to raise this amount.

The plant will process foods, chemicals, plastics, and medical equipment with gamma radiation. Gamma Process Co. has announced that this will be considered a production facility and that its plant in Chicago will continue to do research and pilot-scale work. The New York plant will be designed for 1 Mc of ^{60}Co, although operation will start with only half this amount; the Chicago plant has a 100-thousand-curie ^{60}Co source.

Canadian Calls for International Coordination on Food Irradiation

K. F. MacQueen, Atomic Energy of Canada Limited, speaking at the recently held general conference of the International Atomic Energy Agency (IAEA), called for greater international coordination of all food-irradiation programs. His reason: this would help increase the world's food supply, i.e., member states might not duplicate wholesomeness studies and more courses in food-irradiation technology could be offered to developing countries. According to MacQueen, 50 countries are conducting food-irradiation programs and 25 are studying food irradiation to see if they should conduct an active development program. Ideally, the IAEA itself could act as the central international control point.

DID Contractor Wins Award

Dr. Vivian T. Stannett, distinguished professor at the North Carolina State University, has been honored for his work in polymer chemistry as applied to the paper industry. He has been given the first TAPPI Paper Synthetics Division Award by the Technical Association of the Pulp and Paper Industry. Dr. Stannett is a member of the USAEC Advisory Committee on Isotopes and Radiation Development.

RTG's in the Antarctic Proposed by SRI

Stanford Research Institute (SRI) is investigating the possibility of replacing three manned geophysical observatories in the Antarctic by instrumented stations operating with power from radioisotope thermoelectric generators (RTG). Working under a $25 thousand grant from the National Science Foundation, SRI will evaluate current operations and compare them to operations under the proposed system. The full-time use of four airplanes is required to operate the manned stations; SRI estimates that, after four to six flights to set up an unmanned station, only one flight a year will be required.

Irradiation of Food Accepted Slowly in USSR

R. Srapenyants, head of the Radioisotope Laboratory of the All-Union Research Institute for Electrification of Agriculture, has stated in an article in *Pravda* that the use of radiation in the Soviet food industry is growing but that new applications are introduced too slowly. Srapenyants announced the operation of new pilot plants for radiation preservation of fruits and vegetables and the construction of a facility for storing irradiated potatoes in Moscow. Russia already has one installation where grain is treated at the rate of 1100 lb/hr with 10 krads for disinfestation. Srapenyants expects Russia's first mobile irradiator to be built sometime this year. Another nuclear device being tested is a density gaging system that speeds separation of soil and rocks from potatoes during harvest.

Italian Government Petitioned for Potato Irradiation

RADIATOM, a group organized in 1966, has filed a petition with the Italian government for approval of

irradiation of potatoes to inhibit sprouting. RADIATOM is made up of several food companies and SORIN (Societa Ricerche Impiante Nucleari) and exists solely to further food-irradiation research and applications. RADIATOM stands for Associazione Radioconservazione e Affini.

Shorter Version of "Atomic Power Today" Available

Atomic Power Today, a 28-min color film produced by the Atomic Industrial Forum and the USAEC, won international awards; many copies of the film were purchased for use in educational programs. However, a shorter version was in demand for service-club showings and other brief presentations to the general public. That version has been produced and is now available, according to the Forum. The new 15-min version is a complete layman's introduction to the production of electricity from nuclear energy. The price of $50 includes reel and case. For further information, contact Public Affairs and Information Program, Atomic Industrial Forum, Inc., 850 Third Ave., New York, N. Y. 10222.

Eighth Edition of "Isotope Index" Available

The eighth edition of the *Isotope Index*, published by Scientific Equipment Co., is now available. Compiled from the latest suppliers' catalogs and additional data, this guide to the isotopes lists the source of every known commercially available isotope, both stable and radioactive. There are more than 16,000 entries — with 6000 for ^{14}C alone — accompanied by a cross-index of 2000 labeled compounds and complete purchasing data, which include chemical formula, specific activity, supplier, catalog number, and latest price. Information is also provided on available calibration samples, radiographic and therapeutic sources, and AEC license requirements.

The 1967 *Isotope Index* is available from Scientific Equipment Co., Publications Department, P. O. Box 19086, Indianapolis, Ind. 46219 — $10 for regular binding, $12 for hardbound, and $10 for microfiche.

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